REFINER
AND NATURAL GASOLINE MANUFACTURER
A GULF PUBLISHING COMPANY PUBLICATION

VOLUME 11, No. 5 MAY, 1932

EDITORIALS

THE message of Henry M. Dawes, president of The Pure Oil Company, to employes through the May, 1932, Pure Oil News, deserves the attention of the whole petroleum industry, in fact it deserves the attention of men in all industry. His words were:

"If Robert Burns' prayer, 'O wad some power the giftie gie us to see ourselves as ithers see us,' had been granted, he might have met a disagreeable surprise.

"If the composite creature which we call the American citizen were suddenly given the power to see himself through the eyes of the composite world citizen at this particular moment, his self-complacency would receive a real shock. He is like a man fallen from a twenty-story window, who, through the grace of God, has escaped mortal injury. He does not, however, return thanks to a beneficent Providence, but curses the architects who design twenty-story buildings, blames the fire department which did not spread a net under him, and Sir Isaac Newton for the law of gravity. He trembles in an agony of fear and nervous hysteria lest he fall from the dizzy heights of the widewalk on which he stands into the yawning depths of the gutter beside it. It does not seem to penetrate his consciousness that there is only one way to move from the bottom, and that is up.

"The American people have always been the victims of exuberant imagination. They always picture themselves as being "carried to the skies on beds of flowery ease" or headed for economic hells such as Dante never thought of. All too often dream profits and nightmare losses usurp the function of the balance sheet and the cash statement. With eyes turned backward upon the disappointments and tragedies of yesterday, the American people are stumbling blindly and almost unwillingly into happier times.

"Fortunately, hysterics never run a very long course. The hysteria of elevation closed about two years ago, and apparently the hysteria of depression ended some two months ago. The lethargy which follows intense nervous excitement is gradually wearing itself out, and the American citizen is reaching the point where he is presenting a little more dignified spectacle to the world at large."

Thought Must Change

PRELIMINARY figures indicate a material reduction in automobile registration because owners can not afford the license fees, buy gasoline and pay the taxes imposed on gasoline. This is one of the causes for diminishing consumption of the foremost product from crude oil.

Each day 8000 automobiles yield to depreciation and go to the junk heap. With sales below the 3,000,000 annual figure, the junk pile is gaining on automobile ownership. When reduced income forces automobiles to remain in the family garage, gasoline is faced with a double burden of reduced consumption.

Considering all aspects of economic stress, gasoline has fared remarkably well. Its price is low simply because manufacturers of gasoline have not given due heed to economic conditions. Thinking of the 1929 variety will not do for 1932 conditions.

So Far Fine

PRICE advances established in April have held in a style that is a credit to the sanity of the petroleum industry. The industry was put on trial when quotations were marked up on both crude oil and refined products.

Only continued careful handling of commodities as

well as crude oil can maintain these price advances Whatever the price structure, the petroleum industry demands continual reduction of its surplus of both raw and finished materials.

Refiners are in better position to assure this reduction than any other section of the industry. By accepting crude oil properly, they can assist state regulation to keep steady withdrawal on crude oil storage. By making slightly less gasoline than current consumption requires, they can diminish the supply of gasoline.

The whole hope of maintaining these better prices is this artificial control of raw material and finished products. The supplies are so convenient that it will be an easy matter to drive prices even lower than they were in March. Only by refusing to overdraw can the balance be maintained.

Price, Price, Price

ONCE upon a time there was a big oil company executive who complained that at least a material part of the public did not seem to appreciate the fact that the oil industry had spent and is spending millions of dollars on research and development work to keep its products abreast of the times.

"A part of the public buying gasoline and lubricating oil," he said in effect, "seems to want to buy on a price basis only. That part of the public unwisely forgets that more than just the raw material and some labor enters into the right kind of refined products. If gasoline is made to meet modern requirements, engineering expenses must be stood by the refiner. If a safe and sure supply is maintained, again the burden falls on the legitimate refiner. He is the one dependable source of supply when the 'fly-by-night', the 'bootlegger' folds up his tent and disappears. A steady and continued basis of buying on price only cannot but adversely affect your dependable sources of supply. Buy from a company of recognized standing and be willing to pay a fair price."

Before we go any further we would like to know if anybody among our readers will disagree with that sentiment—some of you may differ as to what constitutes "recognized standing" but we are sure that if it is explained that by "recognized standing" is meant any company that conducts its business fairly and offers a product representing its best effort to serve the public, nobody will disagree with the sentiments unless it be he whose own methods are dubious.

All right—we're all agreed!

But what does your oil company official do to set an example?

Does he practice what he preaches?

Some do, but others—ouch!

Listen to what the manufacturers say:

"Oil company buyers generally are beating down the prices on oil equipment to the point where there is absolutely no profit left. If the present bombardment continually to cut prices doesn't let up it will ruin many legitimate manufacturers.

" . . . and some buyers seem to think that when a manufacturer tries to sell them something the only legitimate charges he may include in his product are simply raw material and a little labor. They forget that the manufacturers have spent real money on *their* engineering departments—that most of the finest labor and money saving devices have been developed by the manufacturers' own engineering departments—and yet they beat the price of the product down to the point where engineering expense cannot be considered. The net result will be to affect progress in equipment."

"The dog-eat-dog policy of many oil company buyers is going to affect adversely the sources of supply for the companies themselves," says another. "There is a market for several million dollars worth of pumps in the oil business even in a year like this—yet the way buyers are buying the pump manufacturers are losing money hand over fist.

"Bootlegging of equipment is actually being encouraged. Quality is being lost sight of in the shuffle. Price, price, price—that is the one god now. The standing of a company, built up by years of painstaking effort and right living goes for nothing. It's price, price!"

What does your purchasing agent think? "You can't quote me but—I'm buying under instructions to get what we need as cheaply as possible. I know our company has bought a great deal of equipment this year at prices that spell ruin to the manufacturers selling it. What can I do? I'm under orders. It is price, price, price."

Natural Gasoline Association

ONE organization that well justifies its existence is the Natural Gasoline Association of America. The scientific development of the industry over a decade is marked by the milestones of the annual meetings of the association. Natural gasoline is a better product because this body has devoted sensible effort toward bringing that about.

The individuals who compose its membership are a harmonious group. Its deliberations have been free of jealousies and bickering. The annual meetings are so conducted that they are a credit to the whole petroleum industry.

Just as there was need for the association when it was formed, there is need for it today.

Hold What You've Got

THERE is both hope and fear in the price structure of the petroleum industry. Hope runs high that the increased quotations can hold; fear exists largely from the efforts that are being made to carrying a rising market beyond its logical level. What comes about will result largely from the wisdom displayed handling a situation that is in such delicate balance that even slight tampering will wreck a foundation, only partly built.

Less than a year ago the industry was a supplicant for what it now enjoys. The producer desired nothing more than a dollar a barrel for his oil. Refiners wanted only a slight profit, while the sales division asked only for prices which would avoid losses.

It is little short of a miracle that such prices have come into existence. The producer can have his dollar for choice oil. Gasoline prices are such that refiners must be slightly over the line in profit territory. And the gasoline consumer knows that service station prices have moved forward.

The inconsistent thing is that the men who begged for just such conditions a year ago now carry a defiant attitude as they wait for still higher prices. Fear rules for what talk and actions of such men may bring.

The price structure of no product will bear abnormal boosting. Gasoline will not tolerate it for two reasons. Behind it there still exists a supply of crude oil sufficient to crush a gasoline market lower than it has yet fallen. Neither will that patient American public tolerate a continued climb in retail prices. Other products are not moving into higher price ground and gasoline will do well to hold what it has gained.

What the petroleum industry should do is to strive to maintain the progress that has been made since April 1, 1932. Only sensible maintenance of supply against demand can accomplish that desirable result. The present price structure should be held for a year if necessary. It should be held until changes in fundamental conditions demand higher prices. There is no question about part of the move into higher level being by artificial means. Fundamentals did not demand it.

On the favorable side there is evidence that the petroleum industry is beginning its house cleaning task. Mergers and large scale purchases are evidence of this. The Sinclair-Prairie merger and the sale of foreign properties of the Standard Oil Company (Indiana) to Standard Oil Company of New Jersey are instances of what is being done in preparation for the next cycle of prosperity for oil.

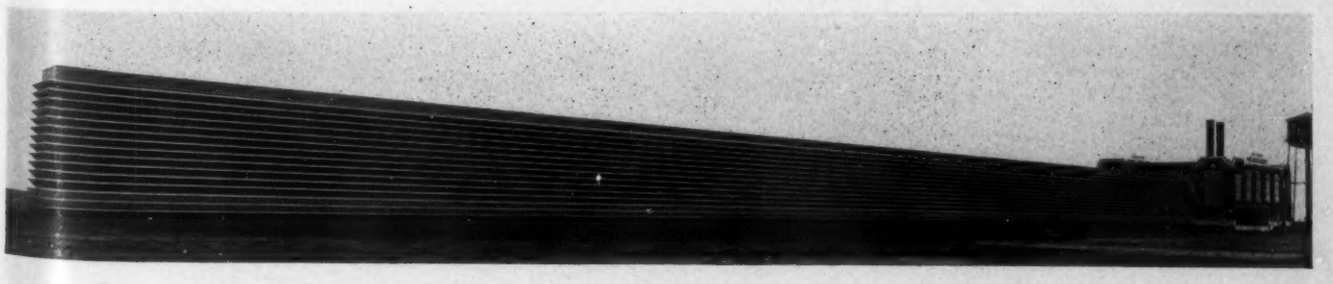
No doubt there is some more of this work to be done. It is not conceivable that all the units which now compose the petroleum industry will retain their identities through the most severe depression of a generation. Concerns in weakened financial condition will have to have the protection of those with surplus funds. The industry will not be ready for its long upswing until these details have been adjusted.

Until all that has come about the one need is to hold what has been gained. Price increases that fail to hold are worse than no price advances. In addition to returning the need for red ink they shatter confidence.

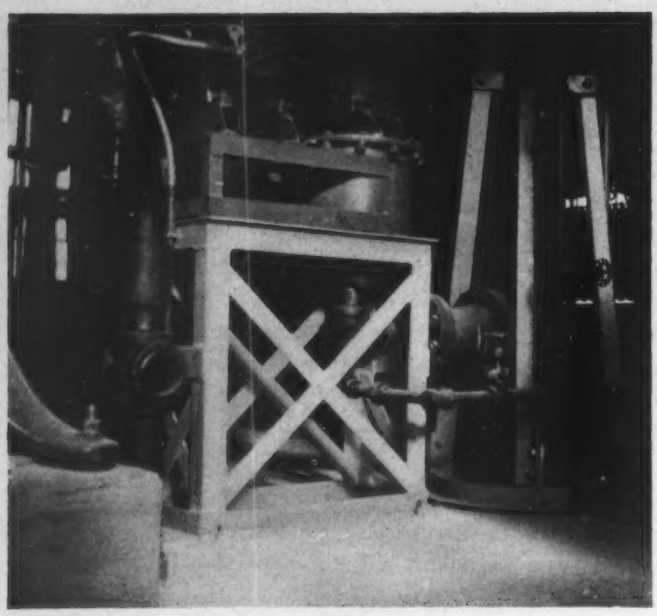
Just as it was foolhardy for petroleum products to sell at the low levels of a year ago, it is more foolhardy to strive to push quotations beyond their present levels. By conservative management the petroleum industry may return a profit at present levels. That is sufficient for this period. Losses are the common result from all business effort today. The industry showing even slight profit is in an enviable position.

It is a long road back to those choice years prior to 1930. Those carefree periods may never return, for profit came easily then and there was little attention given to the conservation of capital. But there will be periods of profit for oil as for other business endeavor. It is just that profit should return only to those with wisdom and energy sufficient to guide their affairs properly.

Unwarranted price boosting may involve energy but it does not include wisdom.



Largest Centrifugal Separator *Sludge Removal*



Turbo Mixer—Acid Inlet in the Bottom

WHEN Raffineries De Petrole De La Gironde, Bordeaux, France, decided upon erection of its refinery several years ago company engineers were sent to America to study and decide upon proper equipment for the plant. These men purchased the most modern equipment available at that time, and after carefully analyzing the trend, in many cases contracted for facilities more advanced in design than that employed by American refineries. The investigation was carried out in colaboration with engineers of the Bethlehem Steel Company, who designed, erected, and started operation of the complete refinery. They erected the world's largest pressure distillate acid treating plant, designing it in such manner that it became sufficiently flexible to treat a pressure distillate derived from any crude produced in the world. The source of crude supply for the French refiner at present is "where he can buy the cheapest," but eventually he will get crude from some of the many French colonies. Under these conditions the engineers decided upon the purchase of a continuous acid treating process involving centrifugal separation of acid sludge.

The requirements dictated that a plant be designed capable of treating, and finishing without re-running, 10,000 barrels per day of 180°C. (356°F.) end point distillate. In comparison, it is thought that the largest similar plant of this type in this country, is located at East Chicago, Indiana, and has a capacity of approximately 5000 barrels per day. It was the writer's good fortune not only to assist in the designing of the French installation, but also in the installation, and to have complete charge of the operation for some time.

OPERATING SYSTEM

The acid separators, together with the necessary pumps, clay feeder, and clay storage, are housed in a two-story building. The acid separators, acid proportioning pumps and filters are located on the second floor, and the clay feeder and other equipment on the ground floor.

Centrifuge Battery

Tracing the flow sheet through the plant it is necessary to start with the charging pump, which is a Goulds centrifugal, the discharge from which is split into three streams, and charges the three centrifuge batteries of five machines each. The plant is so designed that it can operate with one of these batteries, or can employ all three.

The amount of charge

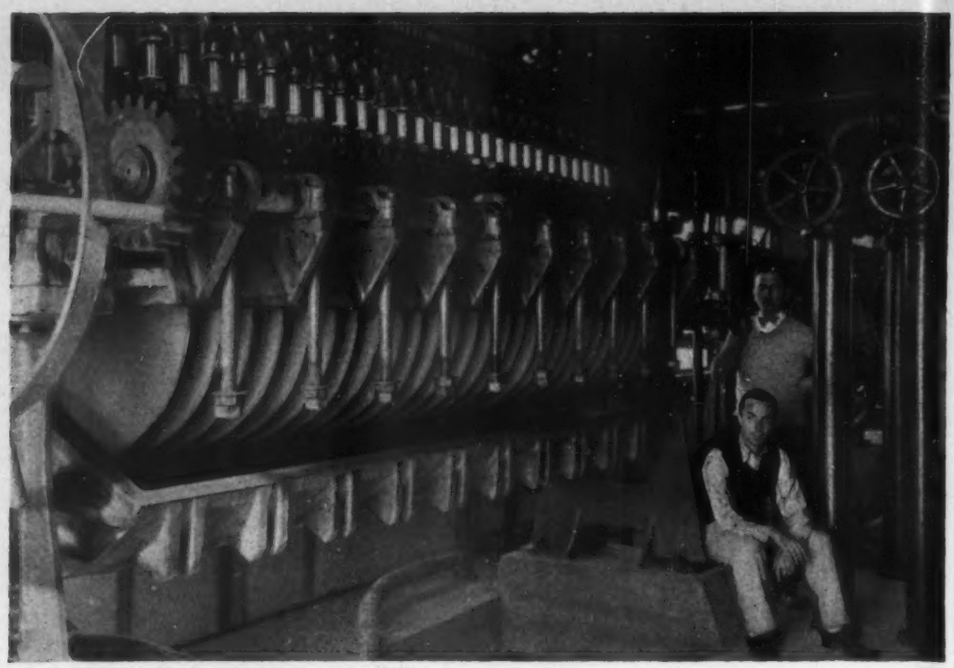
Plant *for Acid* Designed For Flexibility

HERBERT TRIVAL

Sweetening Plant Chemical Mix Tanks

is measured by direct-reading flow meters, calibrated in cubic meters. The pressure distillate passes through two sets of mixers. The first consists of three six-inch Duriron stationary mixers, and the second is a Turbo mechanical mixer. The design calls for two mixers for the reason that a large range of contact time is desired, and further to allow a two-stage treat, such as a pre-sludge treat, followed by a strong acid treat, if desired. The acid proportion pumps are installed near these mixers, and there are two pumps for each battery of centrifuges. The pumps are Hills-McCanna proportioning

Transfer Pumps on the Ground Floor

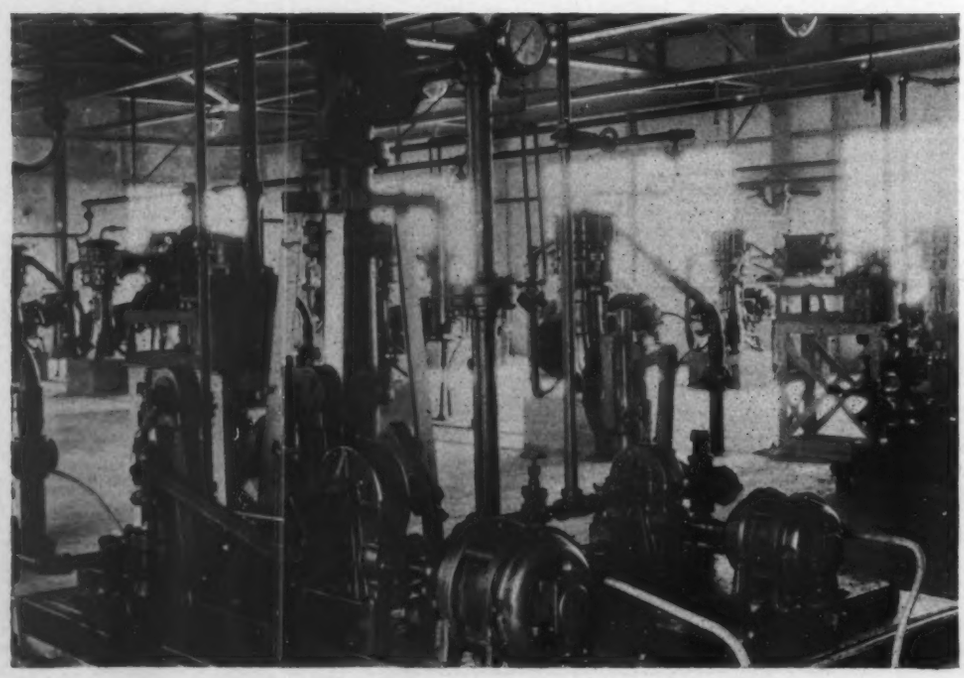


Filter Press located on the Second Floor

type, fabricated of Duriron metal. These pumps are manifolded to the mixers in such manner that the acid may be applied to each mixer, or that sludge acid will reach the pressure distillate ahead of the stationary mixer, and the fresh acid just ahead of the mechanical mixer.

The acid pumps take suction from constant level tanks installed on the same level with the pumps. On the suction side of these pumps are installed three-way Merco cocks. Extending upward from these cocks are gauge glasses showing the height of the acid in the feed tanks. By turning the cock so that the pumps take suction from these gauge glasses, it is possible to determine the amount of acid being pumped. This simple device also acts as a tell-tale for the operator, enabling him to tell at a glance if the pumps are delivering acid to the mixer at a constant rate.

From the mixers, the acid and pressure distillate flows directly to the centrifuges. The sludge is completely and instantly removed from the distillate, and flows to storage by gravity, and eventually is evaporated under the power house boilers. The distillate flows to the slurry tank on the ground floor, and as it enters this tank, a pre-determined amount of 200-300 mesh clay is applied to the stream. The distillate is in a slightly acid state at this stage, which increases the absorbing power of the clay to a remarkable degree. A centrifugal transfer pump transfers and assists in the mixing of the clay and dis-



Acid Pumps and Mixers

tillate. The slurry is kept in agitation by mechanical means in an agitator not less than four minutes, and is then filtered.

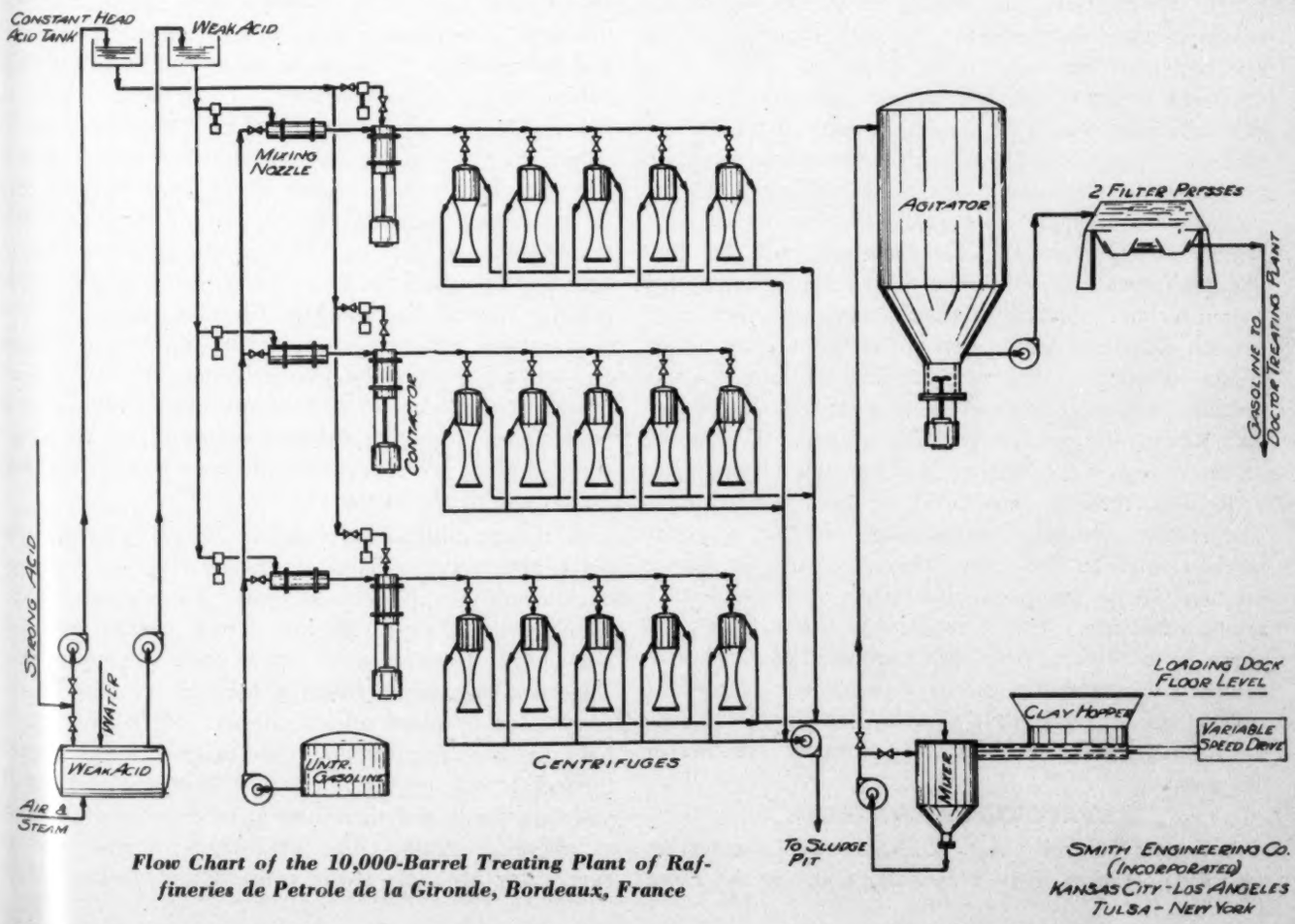
The filters, of which there are two, are Sweetland type with Monel metal cloth covered leaves. They are so manifolded that it is possible to change the flow of gasoline from one to the other without interruption. Each filter will hold 1000 pounds of clay before it is necessary to clean. In a short time, the French operators were able to shut down and clean one of these filters in 18 minutes. Air was used to blow the cake dry; 500 cubic feet per minute was found to give the best results. The filters were mounted on the second floor, at one end of the building. Beneath the filters, a metal chute extends outside the building at a 70 degree angle. The spent clay from the filters slid down this chute into small dump cars. A spur of the industrial narrow gauge railroad runs under this chute. When four cars are full of spent clay, they are hauled away and dumped.

From the filters, the gasoline flows to a 500-barrel run-down tank. The sweetening plant charge pump takes suction from this tank continuously, and the gasoline is sweetened together with the straight-run gasoline and sent to storage ready to be loaded.

At first glance, it might appear quite a problem to get all phases of this plant running at the same throughput, but as a matter of fact, it proved to be a very simple operation. The centrifugal charge pump was the leader, and the rest of the pumps set to operate at the same rate.

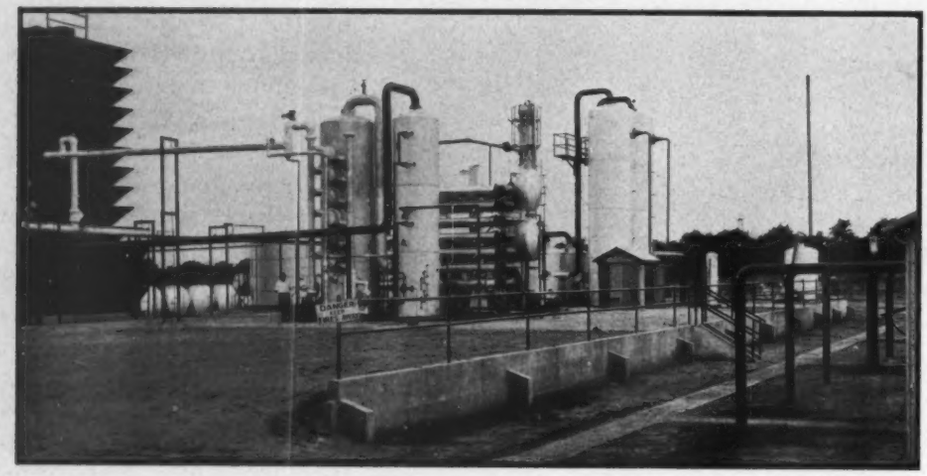
It was found that the best results to be obtained with the pressure distillate produced at this time required eight-tenths of a pound of 66 Baume acid per barrel of pressure distillate, acid applied at the mechanical mixer only. The time of contact before complete separation was three seconds. Eight-tenths of a pound of clay was used. This clay was a French product, and much inferior to our Florida or similar clays. The pressure distillate before treating was 16-18 color; after treating, 28-30 color, and stable after setting 30 days in front of a window. The loss from treating was so small that the accounting department had difficulty in giving a reliable figure due to the normal error of gauging. It was eventually set at one-half of one per cent. This low loss is not surprising to men who are familiar with this process of treating. Chemists have found that the amount of oil in acid sludge from an ordinary settling process will average about 67 per cent of 28 gravity oil. Oil found in the sludge from a centrifuge will average about 26 per cent of nine gravity.

In this treating plant, the operator has accurate control of amount of reagents, time of contact, and actually wrings the sludge free from pressure distillate. The plant attracted a great deal of attention in Europe. Refinery operators visited it from several countries, and were enthusiastic about the appearance and operation.



Flow Chart of the 10,000-Barrel Treating Plant of Raffineries de Petrole de la Gironde, Bordeaux, France

Proper Placing of Control Instruments for Efficiency



D. E. FIELDS

Chief Engineer, Tulsa Boiler & Machinery Company

ON some of the later installations of natural gasoline plants, several changes have been made over previous installations in the placing of the various control instruments, and such changes tend to give better efficiencies of plant operation.

On the larger plants, for example, two absorbers are generally used with each distillation unit and these absorbers are tied together in such manner that a certain predetermined oil level is maintained in both. One of the new features of this plant is the installation of a remote control valve on the absorbers with the diaphragm valve on the discharge side of the rich oil pump. Steam turbine driven centrifugal pumps are widely used for the oil pumps and are shown on the accompanying layout—Figure 1. The rich and lean oil pumps in this installation, are identical and have a capacity of 400 gallons per minute against a 250-foot head. The piping on the pumps is arranged so that the rich oil pump can be used for the lean oil pump if the latter is shut down. The remote control valve maintains absorber pressure on the rich oil pump suction, which decreases the pumping head on the pump and this results in a considerable saving of steam. This arrangement also prevents the pump from "kicking-off," as sometimes happened with ordinary liquid level controllers placed on the absorbers. If the oil level in the absorbers suddenly dropped, the balanced valve would close, cutting off suction to the pump.

EVAPORATOR CONTROL

A remote control valve is also used in connection with the operation of the evaporator unit. In the Tulsa Type design of evaporator, for example, the column has six bubble trays with a built-in heating element above each tray. The elements have removable tube bundles. The steam enters the six elements in parallel and passes down through the tubes and back and then enters the condensate header. From here it goes to the boiler house. With this type of evaporator oil enters the first heating element and then spills out onto the top bubble tray, here the lighter vapors held in the oil are vented, the top part of the evaporator serving as a vent tank. The oil flows across the top tray and then into the downcomer, entering the second heating element from below. It then passes through this element and comes out of the top of the element and spills over onto the second bubble tray. Vents are placed in each element so that any vapors released will pass on up through the bubble trays. The oil passes through all of the elements in the same manner and into the bottom of the evaporator.

A remote control valve holds the oil level and the diaphragm valve is placed on the lean oil line from the exchangers into the lean oil tank. This causes the exchangers to always run full, which results in much better heat transfer than where flow is intermittent. Superheated exhaust steam is used in the base of the evaporator in place of live steam. Back pressure is held on the turbines and this exhaust steam passes through a superheater where it is dried out and heated with live steam and then introduced into the evaporator as agitation steam. The advantages of this type of evaporator are: less steam consumption, less radiation

loss, less equipment to insulate, a lower construction cost and a simpler and more compact unit.

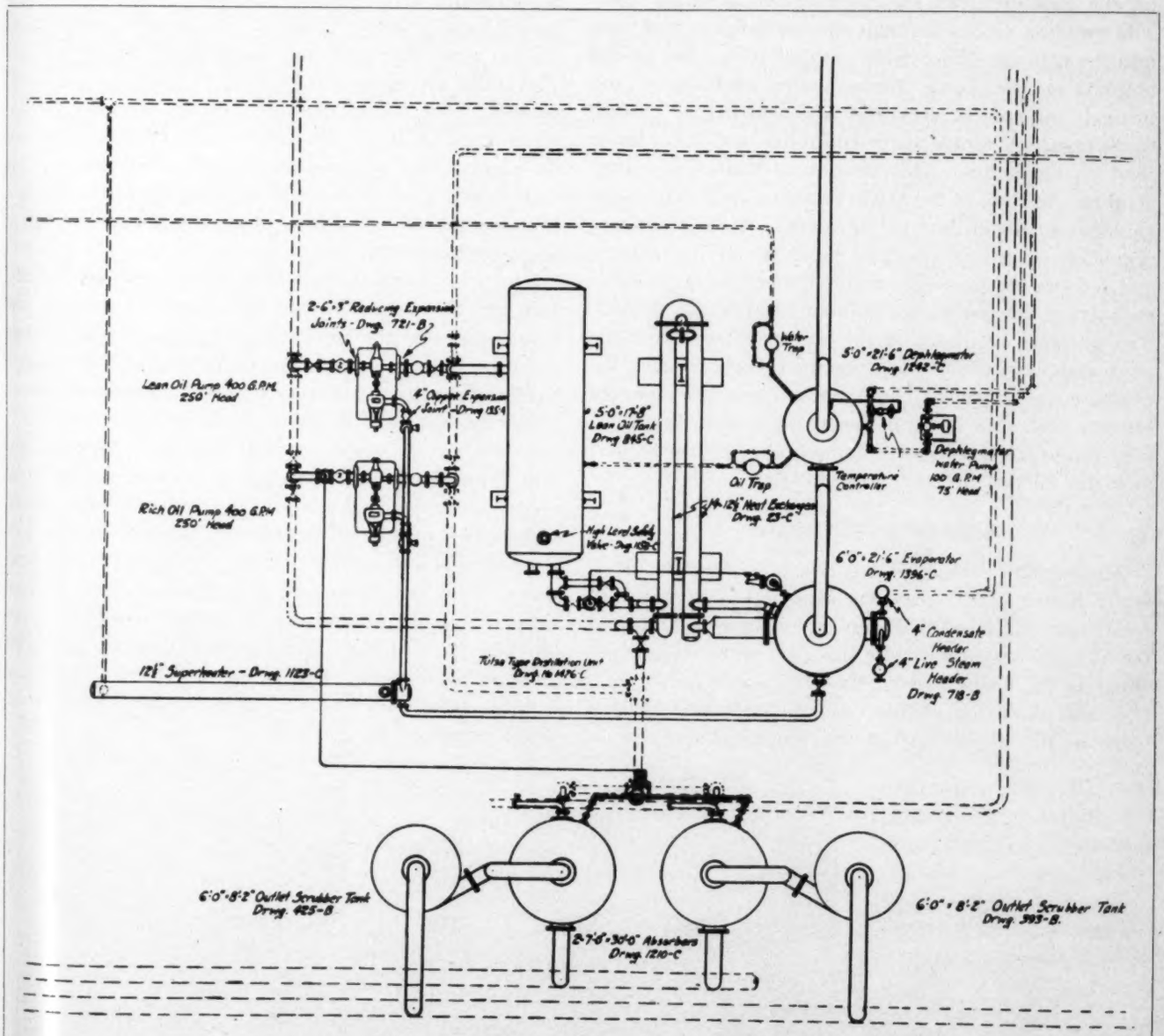
With the remote type of controller the lean oil is several degrees hotter leaving the base of the evaporator due to no expansion taking place as the oil leaves the evaporator. With former practice the oil was subjected to some cooling as it passed through the balanced valve and the pressure was reduced.

On the reflux line into the dephlegmator a temperature controller is used which holds a certain predetermined temperature on the top tray of the dephlegmator. This instrument can be hooked up so that if the temperature on the top tray rises, the valve will open, permitting more reflux to pass, or it can be set in the by-pass line and if the temperature rises on the top tray the valve will close in the by-pass, forcing more reflux into the tower.

A five-tray dephlegmator is used which has a mist-extractor in the top and a water compartment about half way down the column. Water or gasoline can be used as reflux. Generally, water is used. A small centrifugal pump takes suction from the water compartment and this hot water is cooled in one section of open type cooler in the cooling tower. After being cooled it is introduced on to the top tray of the dephlegmator and the temperature controller on this line holds a certain temperature in the top of the tower. A water trap and an oil trap are tied into the bottom of the dephlegmator; the oil trap discharging into the lean oil tank and the water trap discharging into the feed water heater.

TEMPERATURE RECORDS

Several temperatures at various points in the plant should be recorded. A recording thermometer should be used on the lean oil line into each absorber. The temperature in the base of the evaporator should be recorded and the temperature on the top tray of the


2-6"-5" Reducing Expansion Joints - Drwg. 721-B
Lean Oil Pump 400 G.P.M. 250' Head
4" Opposite Expansion Joint - Drwg. 1554
Rich Oil Pump 400 G.P.M. 250' Head
12½" Superheater - Drwg. 1123-C
5'0"×17'8" Lean Oil Tank Drwg. 845-C
High Level Safety Valve - Drwg. 150-C
Water Trap
Oil Trap
No. 12½" Heat Exchanger Drwg. 23-C
5'0"×21'6" Dephlegmator Drwg. 1242-C
Temperature Controller
Dephlegmator Water Pump 100 G.P.M. 75' Head
6'0"×21'6" Evaporator Drwg. 1396-C
4" Condensate Heater
4" Line Steam Header Drwg. 718-B
Tulsa Type Distributor Unit Drwg. No. 1476-C
6'0"×8'2" Outlet Scrubber Tank Drwg. 425-B
8'7½"×30'0" Absorbers Drwg. 1210-C
6'0"×8'2" Outlet Scrubber Tank Drwg. 393-B.

Tulsa Type Absorption Gasoline Plant, Showing Control Instruments

dephlegmator should also be recorded. Usually a combination recorder and controller instrument is used on the dephlegmator reflux line. Various pressure regulators are needed on the incoming gas line to the plant and on the residue gas lines from the residue scrubbers. A regulator on the fuel line to the compressors is also required.

At the fractional distillation column a number of control instruments are required. The column as shown in the drawing is a high pressure fractional distillation column of conventional design, having 30 bubble trays. A kettle 36 inches diameter by 20 feet long is used. The reflux condenser is placed on top of the column and the reflux is fed onto the top tray by gravity. Six four-inch gasoline heat exchangers and four four-inch gasoline coolers are used in this installation. A constant speed pump governor controls the speed of the feed pump which makes the feed to the column constant.

On the larger installations a flow controller is used on the gasoline feed line to maintain constant feed. The gasoline passes through the exchangers and then into the column. The stable gasoline passes out of the bottom of the kettle through the exchangers and through the coolers, where it is cooled before passing to storage. A temperature controller and recorder is used on the kettle. This instrument maintains a constant temperature in the kettle by operating a diaphragm valve in the steam line to the kettle. A back pressure regulator maintains constant pressure on the column and reduces the pressure on the lighter and undesirable ends from the top of the column to about 25 pounds. The pressure regulator at the boiler house, where the light ends are usually consumed as fuel, reduces the pressure on down to the required pressure for the burners under the boilers. Generally a recording pressure gauge is used on the column and a recording thermometer on the top tray of the column.

BOILER REGULATION

Another new feature of this type of plant is the feed-water heater which also acts as a water purifier and condenser. It is of the open type. Direct contact of the exhaust steam with the make-up water is brought about in the lower part of the feed water heater by a tray and deflector plates. Aerial condensation takes place in the upper part of the heater in the nest of tubes exposed to the breeze. In the top there is a mist-extractor to prevent carry-over of the liquid. A balanced valve on the make-up water makes the heater automatic in operation. No pressure is held on the feed-water heater, as it is open to the atmosphere. The water from the water trap on the dephlegmator is introduced into the heater near the bottom. All exhaust steam from various pumps and turbines (excess steam over that required in the evaporator) is introduced through a large opening near the top of the bottom compartment. The temperature in the bottom is approximately 190° F. and a feed water pump takes suction from the bottom of the heater and discharges into a mixing tank which is under approximately 150 pounds when operating the boilers at 175 pounds steam working pressure.

The condensate from the evaporator heating elements is also introduced into the mixing tank and these two streams are mixed. The pressure on the heating elements is used to force the condensate into the tank and no pump is necessary on this service. The resultant temperature, after mixing the two water streams is approximately 260° F. and a feed-water pump takes suction from this tank and discharges into the boilers. The steam saving on this hook-up is obvious. The condensate from the evaporator heating elements is approximately half of the feed water requirements for the plant. This water is under just a few degrees less than boiler temperature and in order to form steam it is only necessary to add a few B.t.u.'s plus the latent heat of evaporation.

The scale forming impurities most prevalent in surface and well water are the carbonates of calcium and magnesium and the sulphates of calcium. The calcium sulphate is by far the most harmful and will form a hard scale. In the presence of other substances, which would be harmless by themselves, it reacts chemically and forms very dangerous scale deposits. Above a certain temperature the solubility of calcium sulphate decreases with an increase in temperature of the water, and at 250° to 260° F. the calcium sulphate held in suspension is practically nil and will precipitate out of solution. After the carbonates and sulphates have precipitated out in the mixing tank they may be easily blown out and the soft clear water is left to enter the boiler. Feed water regulators are used on the boilers, maintaining the water level by controlling the speed of the feed-water pumps.

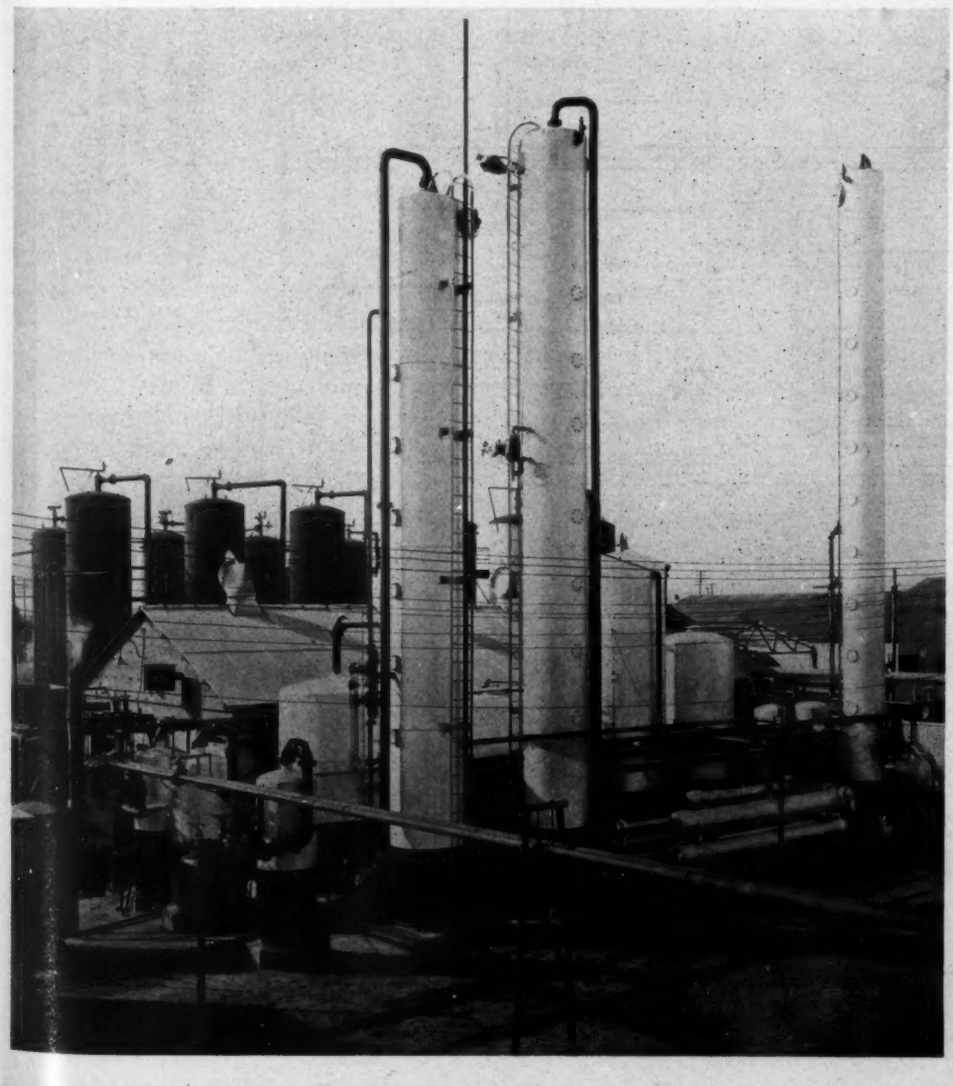
Reflux Ratio Determined *by* Volume *of* Stabilizer Charge . . .

J. C. ALBRIGHT

AFTER having redesigned the flow through the Dubbs units whereby the throughput through the cracking plant was about doubled in volume, the vapors resulting from this new operation, and the added volume of pressure distillate produced made it necessary for Producers and Refiners Corporation, West Tulsa, Oklahoma, to install a combination pressure distillate rectifying plant and a gasoline recovery unit with a final product stabilizer. Burrell-Mase Engineering Company designed and fabricated the various units entering into the system. Three reasons are given for the installation of this type of equipment: first, processing the raw pressure distillate in order that treating of it through acid contactors might be simplified and carried out with small losses. Second, to recover the vapors from the various rundown tanks, etc. Third, to install equipment so designed that a minimum amount of operating difficulties and supervision might be required.

The crude passed through the first operation runs about 39.9 degrees A. P. I. and is processed through a 6000-barrel skimming plant designed by Winkler Koch Engineering Company of Wichita, Kansas. This unit strips the charge down to 25.6 A.P.I. gravity reduced crude as charging stock for the Dubbs, and is then processed through them in recovering pressure distillate, coke and gas.

The characteristics of the plant pressure distillate are normal and run consistent with that produced at other plants with charging stock of the same quality. Normal or possibly less amounts of light vapors result from the skimming operation. Pressure distillate produced after condensation is received in a PD drum placed just outside the control room of one series of the cracking units. A pressure of 90 pounds is carried on this receptable and the pressure distillate



Gasoline recovery plant of Producers & Refiners Corporation, West Tulsa.

BURRELL-MASE ENGINEERING CO.
PITTSBURGH, PA.
FLOW DIAGRAM
P.D. STABILIZER AND ABSORPTION PLANT
PRODUCERS & REFINERS CORP.
WEST TULSA, OKLA.
Final Stabilizer Reflux Pump
Reflux Condenser
Reflux Condenser Accumulator Tank
Final Stabilizer and Base Heater
Gasoline Cooler
Gasoline Heat Exchanger
Final Stabilizer Charge Pump
Level Flow Ratio Control
Gasoline Preheater
Surge Tank
Main Condenser
Main Condenser Accumulator Tank
Dephlegmator Pump
Stripped Oil Tank
Stripped Oil Pump
Oil Cooler
Oil Heat Exchanger
Still
Charged Oil Pump
Absorber
Scrubber
Main Inlet Drip
From Dubbs Pressure Sources
Absorber Drip
P.D. Reflux Condenser
P.D. Accumulator
P.D. Reflux Pump
Tail Gas Cooler
P.D. Stabilizer and Base Heater
Level Flow Ratio Controller
Compressor (Gas Engine Drive)
Vacuum Regulator
Suction Drip
Indicating Vacuum Gauge
From Gathering System
P.D. Preheater
P.D. Heat Exchanger
P.D. Cooler
P.D. Charge Tank
To P.D. Storage
Raw P.D.
To Fuel
To Gasoline Storage
To Tank
Steam
Meter

leaving it to the stabilizer is reduced at the base to 65 pounds gauge. As the production of pressure distillate varies in quantity as the units are placed on stream or blown down, the quantity delivered to the stabilizer also varies in direct proportion to the production. To prevent the fluctuation of base product in regards to quality, two things were necessary. Either an operator must be stationed at the column to control the reflux in constant ratio to the raw PD feed, or instruments doing that duty automatically must be installed. To put the stabilizer column on positive automatic control, Mr. Mase and Metric Metal Works worked out a combination of instruments that control the reflux ratio in direct proportion to the feed stock entering the stabilizer column.

Three instruments were utilized to work in co-ordination with each other. The master instrument, a Westcott orifice meter, was set in the line as it leaves the pressure distillate drum, while the other two, one set on each side of the master instrument, are rate volume controllers, controlling valves set in both the PD charging line and the reflux line leading to the top of the column.

The first instrument is essentially a wide range liquid level indicator, showing on the chart of the recorder the level of the pressure distillate as it is in the drum. As this level raises, due to increased production, or falls for any reason, the point of level is recorded on the chart. The actuating linkage operating the two instruments placed on each side of the master meter is connected to the pen arm of this meter. When the drum begins to fill, this condition is instantly shown on the center instrument and as the pen arm moves across the chart, it operates the other two instruments. The motor valves in these two volume rate controllers open the control valves on the raw PD charging line and the valve on the reflux line admitting the required amount of pressure distillate to maintain a predetermined level in the drum, and as the rate of charge is accelerated, the amount of reflux to the top of the column is also increased. The ratio between reflux and raw feed is variable, but when the two instruments are calibrated to the desired amount the ratio remains constant. As the rate of production declines, the instruments admit less pressure distillate to the column, and at the same time less reflux is pumped to the top. It does not matter if the production in the PD drum increases rapidly, the predetermined rate of reflux in the desired ratio to the raw charge is always delivered to the top of the column. By using these instruments, constant base product characteristics are uniformly maintained.

As this raw pressure distillate is delivered to the column under reduced process pressure, it passes through the controlling valve into two sections of Griscom-Russell Vaneflo heat exchangers in counter current to the finished product drawn from the base of the tower. Superimposed upon these heat exchangers is one section of preheater where the charge is given a preliminary temperature of 250° F. A Foxboro temperature rate controller with the valve placed in the steam line leading to the preheater, admits as much steam as is necessary to attain this temperature. Just as it enters the section it is dried of all condensate by the utilization of Armstrong steam traps, thus preventing passing unnecessary volumes of water through the apparatus.

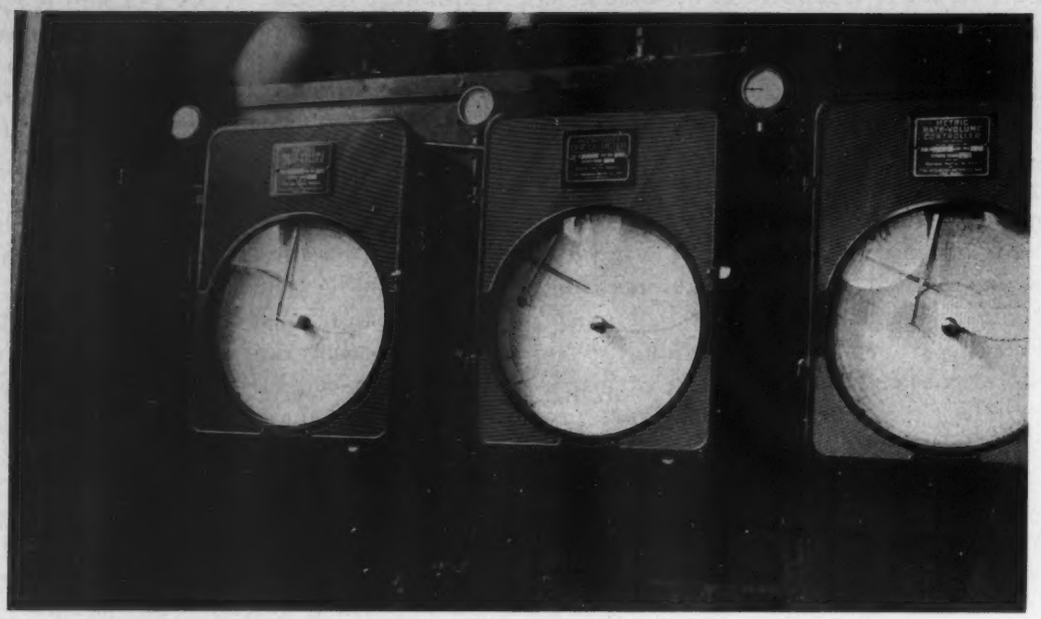
As the feed stock is admitted to the column it flows downward over the bubble caps which are peculiar in construction to Burrell-Mase engineering. Five caps are built into one major unit having serrated edges cut in the projecting rims placed on the under side of the caps. Suspended baffles are placed between each serrated ring and the one adjacent to it which gives the ascending vapors and the descending PD a turbulent action. The down comers are suspended from the outer rim of the cap plate and extend to the top of the one below, but are not sealed in wiers. Instead, swing flaps are connected to the lower end of these spouts which close the opening except during the time that oil is circulated.

As the pressure distillate in process reaches the base of the column, it is automatically transferred to the reboiler section placed outside the column, but quite close to it. It circulates from the base through this apparatus and back to the tower. A temperature of 314°F. is maintained on the base of the column and the steam used for this purpose is admitted to the reboiler as it is required by a Foxboro temperature rate controller in the same manner as that used on the preheater. Any base temperature may be maintained at the predetermined point within the limits available through the properties of the steam used.

Those vapors extracted from the pressure distillate in process are essentially propane, but with the rate volume controllers set at the proper point, any cut may be taken from the overhead stream even down to and including pentane. The vapors rising through the length of the column, driven from the PD by the heat applied in the preheater and base heating element are refluxed at the top of the tower by pumping the condensed overhead cut back over the tower. With this equipment the fractionator top temperature is not regulated but remains uniformly constant by pumping the proper amount of reflux over the tower to provide the desired base product.

The stabilized pressure in the base of the column is removed under process pressure through the heat exchanger and a series of cooling coils. After the desired temperature is reached, the finished product passes through a Neilan control valve actuated by a liquid level controller placed on the side of the tower. The rate of removal is constant and in direct proportion to the feed entering the column in the first steps of the process. After it passes through this valve, it is led to the proper storage after which it passes through the plant treating system for the removal of the undesirable properties contained in it.

The overhead cut from the column is cooled and con-



Rate volume controller at P. D. stabilizer in plant of Producers & Refiners Corporation plant at West Tulsa.

densed and afterwards received in an accumulator tank set near the base of the tower. Liquid for reflux is drawn from this tank through a connection placed some distance from the liquid level control float so that there is no danger of the pump becoming gas bound by taking suction from the upper level of the liquid in the tank. Excess volume over that required for refluxing the column is trapped through this liquid level control and sent to the surge or mixing tank at the gasoline vapor recovery plant. Those vapors coming over with the top cut but which are not condensed into liquid form are permitted to escape from the accumulator tank through a pressure rate controller which maintains a constant pressure on the tank. These vapors are led to the gasoline plant to be processed in extracting the remaining desirable fractions.

The gasoline recovery plant to which the vapors and overhead product from the PD stabilizer are sent consists of three major units; absorber, still and final product stabilizer. These vapors as well as those from the skimming unit, rundown tanks and loading rack are all processed in a blend through this plant. Those vapors which originate at sources not having enough pressure to pass them through the absorber are gathered and brought up to process pressure through a Clark 65 horsepower gas engine with a 15½ by 20-inch cylinder. All the gas which is processed is passed through a main inlet drip, a small vertical tank set near the absorber. It was set to remove from the gas stream all condensate which may accompany it to this unit. After passing through this tank, the gas is led to a larger vertical tank in which a lime solution is maintained through the mass of which the vapors and gas are required to bubble extracting the hydrogen sulfide before it passes to the absorber.

In the line between this scrubber and the absorber, an orifice plate in a flange was placed to which connections were made to a Foxboro ratio controller. After the gas enters the absorber column, the travel is the same as in other units of this general character. As it leaves the top of the tower, the gas is led downward to a small residue scrubber set beside the main inlet drip. On the outlet of this residue scrubber a Neilan back pressure control valve is located, operated by a Neilan control instrument placed on the main control board in the pump room. A uniform pressure of 30 pounds is carried on the absorber, that pressure having been found sufficient for complete extraction of the desirable fractions in the gas under process. Passing through this valve, the residue is admitted to the plant fuel lines and is burned for fuel under the stills and boilers in the plant yard together with light uncondensible gas from the Dubbs units.

Lean oil in the system is contained in part in a surge tank and is pumped from this unit by a Worthington two-inch single stage centrifugal pump direct connected to a five horsepower United States 220/440 volt motor. Control of the volume of the oil to the absorber is maintained by the functioning of the Foxboro ratio controller actuated by the differential pressure of the gas passing to the absorber. As the volume of the gas increases, the ratio controller opens a 1½-inch valve set in the line leading to the top of the column. As the volume drops, this valve automatically closes to compensate for the reduced amount of gas passing to the absorber. Any oil to gas ratio may be automatically maintained by manipulation of the instrument. Once this ratio is fixed, it remains constant regardless of the volume of gas being fed to the absorber. In this manner, a constant saturation of the rich oil leaving the

column is secured, providing a positive stripping of the gas to those fractions desired.

The amount of oil leaving the absorber is controlled through the action of a Neilan float set on the side in the regulation manner, but actuating a valve on the discharge line leaving the rich oil pump. This pump is a duplicate of the one in the lean oil circuit, another of which was set to be used as a standby for either circuit. Starting of these pumps is obtained through the operation of Cutler-Hammer oil immersed push buttons placed near the individual motor. As this pump picks up the oil it delivers it through a series of two Griscom-Russell Vaneflo heat exchangers in counter current to the flow of the lean oil from the still. Passing directly to this unit the oil is admitted above the stripping plates without preheating. Entering at a uniform temperature of 240°F., it spills downward over the stripping plates to come in contact with the process steam admitted at the base of the still. This process steam performs a double duty in this still inasmuch as it strips and heats at the same time. Sufficient volume is used to bring the temperature of the oil in the base of the still up to 307°F. The amount of steam required is controlled through the action of a Foxboro temperature controller maintaining the predetermined temperature by the admission of more or less steam as conditions require.

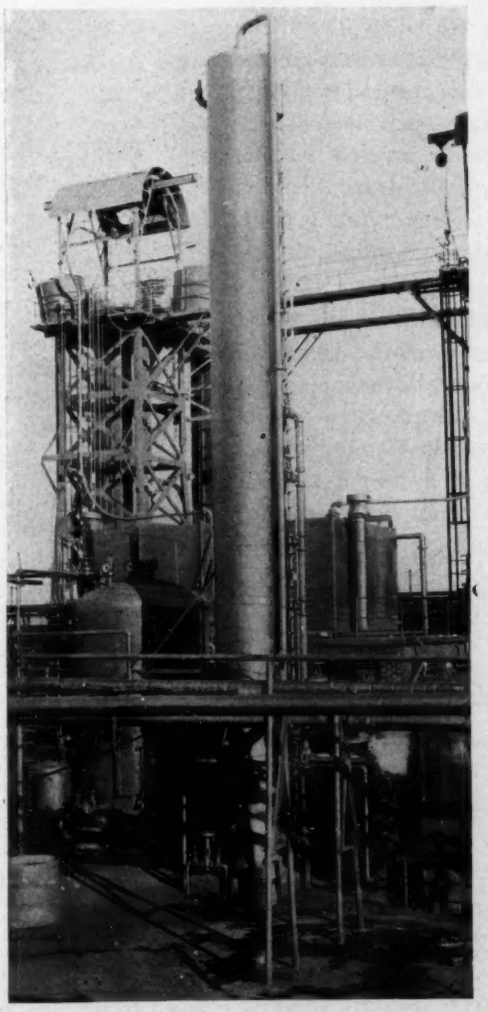
The upper section of the still is utilized as a dephlegmator to reduce the end point of the gasoline recovered from the rich oil. Vapors coming from the overhead line are carried with low end point constituents by refluxing regular absorption "make" over the top of the column pumping with a Dean Brothers close clearance, simplex steam pump. A temperature rate controller actuates a diaphragm valve placed in the steam line leading to the steam chest of the pump so that a temperature of 175° F. is carried at the top of the column.

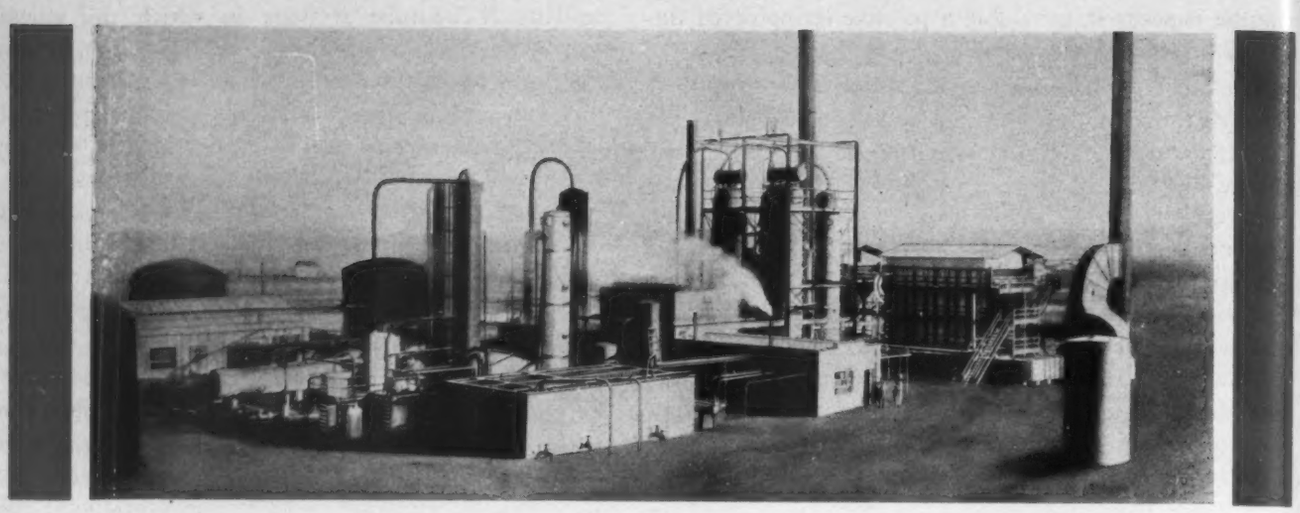
Gasoline vapors after refluxing are carried through Griscom-Russell Bentube sections in which the gasoline is condensed. The condensate is received in an accumulator from which the reflux pump takes suction. Vapors not condensed in this process are passed back to the absorber pressure, that unit being operated at 65 pounds gives it a differential of 32 pounds over the absorber. A Neilan liquid level control permits the condensate in the accumulator tank to be transferred to the mixing or surge tank where this product is blended with the overhead cut taken from the pressure distillate fractionator.

As this mixture of absorption gasoline from this plant and that from the Dubbs sources have a content of lower boiling fractions not desired in the finished product, the entire "make" is processed through the final fractionator of stabilizer. A Dean Brothers pump picks this liquid up from the shell of this horizontal surge tank and directs it through three sections of Burrell-Mase gasoline heat exchangers, then to the final stabilizer column. A Metric Metal Works rate volume controller is placed in the circuit being actuated by the rise and fall of the liquid in the tank. Its action and duties are identical with those of the one placed on the P.D. stabilizer; and as the production of charging stock increases, it also admits more reflux material to the top of the column. A predetermined ratio of reflux to feed is constantly maintained on this unit without attention from the operator.

A column pressure of 190 pounds is maintained with a base temperature of 240° F. Finished base product is removed through a Neilan control valve leading the material through the gasoline heat exchanger and coolers to the proper storage. A production of 8000 gallons daily average is made with this unit utilizing all the vapors from the plant. The overhead cut from the stabilizer is condensed and received in an accumulator tank near that one utilized in receiving the stable product. Those vapors coming from this accumulator are vented to the fuel lines with the remainder of the light gas and residue produced in the plant.

Debutanizer column in the plant of Producers & Refiners Corporation, West Tulsa.





Integrated Units *Controlling More* Refinery Capacity

GEORGE REID
Associate Editor

REFINING capacity continues to shift toward the integrated type of company. Regardless of the economics of the situation, more refining companies are engaging in the marketing of petroleum products, and more refineries are being erected by the integrated type of refining company. And, incidentally, each year more of these station-owning refining companies are expanding refining facilities through the addition of cracking equipment.

An analysis of the industry indicates that the refining concerns still have faith in the original idea that oil companies can sell their products through their own marketing outlets. The fact that the industry admits the presence of too many retail outlets seemingly does not deter new comers in the field, nor does it prevent long established refining concerns from branching out into the marketing of products through company controlled bulk and service stations, and at present, at least one major concern contemplates early entry into this field.

During the past few years refiners have established a definite trend toward the concentration of refining capacity at the points providing largest market for their products, and toward the rounding out of large integrated organizations throughout all sections of the country. This latter type of concern is with each succeeding year becoming more and more in control of the refining capacity of the United States, and at the expense of the "non-retailing" type of refining organization.

Available records as of May, 1932, reveal a total of 280 concerns engaged in the refining of petroleum, and of this number it is known that 135 companies also operate service stations and bulk distributing plants, leaving 145 companies having no retail sales departments. The present motor fuel requirements of the marketing branch of the industry has contributed to the establishment of cracking departments in the plants of 95 of the integrated companies, leaving 40 integrated concerns that have not yet begun cracking. It will be of interest to watch the developments during the next few years in this respect, for the reason that competitive conditions and demand for premium fuels must force some changes in manufacturing methods in this group.

In regard to the steady growth of the integrated type of company, which group apparently desires to continue expansion of marketing outlets and refining facilities, it is interesting to compare the present status against that of 1927 at which time a similar survey of refining and marketing, or integration and non-retailing, was published. (Ref. & N.G.M., June, 1927, page 53.) For the purposes of this and the former discussion a survey was made of the territory termed Mid-Continent and the Chicago territory, to determine the trend of refining capacity. For the years 1924 and 1927 a resume and tabulation of all of the refining companies operating in the given territory was made, separating those which were integrated companies or retailers of gasoline from those which were non-retailers. A similar tabula-

TABLE 1

Refineries Without Company Owned Service Station Outlets
Mid-Continent and Chicago Territories

SECTION	Operating Plants 1932	Capacity Barrels 1932	Operating Plants 1927	Capacity Barrels 1927	Operating Plants 1924	Capacity Barrels 1924	Decrease* Capacity Barrels 1924–27	Decreas Capacity Barrels 1927–32
North Texas	18	48,250	23	67,100	27	74,750	7,650	18,850
North Louisiana	4	8,900	3	16,000	9	27,800	11,800	7,100
Arkansas	8	37,500	7	28,900	10	18,190	**10,710**	**8,600**
Oklahoma	17	61,800	24	53,700	37	142,400	88,700	**8,100**
Kansas	5	42,000	4	14,700	15	69,000	54,300	**27,300**
TOTAL—Mid-Continent	52	198,450	61	180,400	98	332,140	161,740	**18,050**
Chicago Territory	3	9,700	3	4,200	6	24,500	20,300	**5,500**
TOTALS, Mid-Continent and Chicago Territory	55	208,150	64	184,600	104	356,640	183,040	**23,550**
Percentage	..	21.5	..	25.5	..	56.5	.....	.....

* Black figures indicate Increase.

tion and separation was made covering the same territory to determine the status of refining capacity in 1932. As a result of this survey the remarkable growth and development of the integrated company capacity is forcibly presented, as shown in Tables 1 and 2.

In the Mid-Continent and Chicago territory there are 93 companies operating 122 refineries. Sixty-seven of these refineries, with a total capacity of 763,000 barrels, are owned by integrated concerns and represent 78.5 per cent of the total refining capacity of the area under discussion. In 1924, only 36 integrated company owned refineries operated in this area and represented only 43.5 per cent of the total capacity, or but 273,500 barrels. During the past five years the integrated concerns have increased the number of refineries from 55 to 67, have increased capacity over 200,000 barrels, and increased their dominance in percentage from 74.5 to 78.5 per cent. This data is presented in Table 2.

In the same area, and viewing the opposing side of the picture, the non-retailing company owned refinery, has been steadily on the decrease, along with capacity, and along with proportionate growth. In 1924 the number of refineries depending upon the jobber or wholesaler of petroleum products for removal of products from the plants was 104, with a total capacity of 356,640 barrels, or 56.5 per cent of the capacity of the territory under discussion. By 1927 the trend toward integration had decreased the number to 64, the capacity to 184,600, and the percentage to 25.5.

Further development of the integration trend during the past five years has decreased the number of this type of refinery to 55, and the percentage of capacity to 21.5 per cent, notwithstanding a gain in capacity of 28,000 barrels. This gain in capacity is brought about through the establishment of some new refineries in North Louisiana, Kansas, and Arkansas, two of which are strictly producers of asphalt, and one of which is now building. The capacity advantage, meaning as little as it does, will be removed when Standard Oil Company of Kansas carries out its reported plans to enter the marketing branch of the industry. Further, the fact must not be overlooked that the death rate among skim-

TABLE 2

Integrated Refining Companies, Mid-Continent and Chicago Territory

SECTION	Plants Operating 1932	Capacity Barrels 1932	Plants Operating 1927	Capacity Barrels 1927	Plants Operating 1924	Capacity Barrels 1924	Increase Capacity Barrels 1924–27	Increase Capacity Barrels 1927–32
North Texas	13	75,000	10	61,250	9	54,000	7,250	13,750
North Louisiana	4	48,500	4	31,800	1	3,000	28,800	16,700
Arkansas	2	14,500	..	.....	..	.....	.....	14,500
Oklahoma	28	244,500	24	180,200	16	78,500	101,700	64,300
Kansas	10	98,500	8	82,000	5	34,000	48,000	16,500
TOTAL, Mid-Continent	57	481,000	46	355,250	31	169,500	185,750	125,750
Chicago Territory	10	282,500	9	180,000	5	104,000	76,000	102.500
TOTAL, Mid-Continent and Chicago Territory	67	763,500	55	535,250	36	273,500	261,500	228,250
Percentage	..	78.5	..	74.5	..	43.5	.....	.....

TABLE 3

Refining Capacity, Integrated and Non-Retailing Companies in the Eastern States—1932

STATES	Integrated Companies	Non-Retailing Companies
Georgia	9,000	.....
Maryland	50,000	.....
Massachusetts	48,000	.....
New Jersey	290,000	25,000
New York	40,500	.....
Rhode Island	11,500	.....
Virginia	1,500	.....
West Virginia	13,000	3,000
TOTAL	263,500	28,000
Ohio	99,000	3,000
Pennsylvania	210,000	40,000
TOTAL—Ohio and Pennsylvania	309,000	43,000
TOTAL—Both Districts	572,500	71,000

ming plants, or the "turn-over among skimmers" has been unusually high.

The Mid-Continent and Chicago territories have been chosen for this analysis of the trend toward integration for the reason that the Mid-Continent district has always been the principle section of the country given over the operation of refineries by non-retailing companies, or, in other words, the section from which the jobber and wholesaler could secure his supplies. This source of supply has shown a tendency to decrease in importance for the past 10 years.

Taking the industry as a whole, in this country, with its total of 280 concerns engaged in refining, it is interesting to note that there is a total of 125 companies engaged in manufacture which utilize the cracking unit for the preparation of modern high anti-knock motor fuels. Of the total number of companies 145 have no retail sales divisions, and of this number 30 utilize cracking facilities and 115 do not. These 115 companies, and the 40 integrated companies previously mentioned as having no cracking equipment, gives a total of 155 companies manufacturing petroleum products, but not employing the cracking unit, and in the face of present demands of the marketing brach of the industry, and current specifications calling for definite octane ratings of motor fuels, it appears that further application of cracking is necessary. It is going to become increasingly difficult for such refining concerns to find distributing outlets for their products for the reason that present anti-knock requirements or demands are such that skimming operations can not meet them even from the better types of crude especially suited for production of this type of gasoline.

In the trend toward integration the refining concerns of the Mid-Continent and Chicago territories are approaching similar conditions that have existed for many years in other leading refining districts. For example, the Louisiana and Texas Gulf Coast area and the Chicago territory are each 96.6 per cent occupied by integrated company refining capacity. On the Eastern Seaboard 90 per cent of the refining capacity is owned by integrated companies, which is also true of the California refining district. Refining capacity of Ohio and Pennsylvania is 87.8 per cent operated by the integrated type of company. The Mid-Continent territory, including North Texas, North Louisiana, South Arkansas, Oklahoma and Kansas, with total refining capacity of 680,000 barrels, is 70 per cent operated by integrated companies. Details of these areas are presented in Tables 3 and 4.

TABLE 4

Refining Capacity, Integrated and Non-Retailing Companies in Various Territories—1932

AREA	Integrated Companies	%	Non-Retailing Companies	%
Mid-Continent	481,000	70	198,450	30.
Chicago Territory	282,500	96.6	9,700	3.4
Eastern Seaboard	263,500	90.	28,000	10.0
Ohio-Pennsylvania	309,000	87.8	43,000	12.2
California	725,000	90.6	75,000	9.4
Texas-La. Gulf Coast	680,000	96.6	22,750	3.4
TOTAL	2,541,000	87.	376,900	13.

A survey of construction work since the first of this year and that now under way and proposed indicates that by far the majority of such expansion is being carried out by the large complete organization engaged in producing, refining and marketing. The conditions which have brought about the present widespread activity in erection of cracking units and gasoline reforming facilities on the part of those companies owning extensive chains of marketing outlets, likewise affects the non-retailing refining organization, for in order to compete in the market, products of like quality must be made available to the jobber and wholesaler, and independent service station operators.

The Part *that* Regulation *Plays in* Liquefied Gas Plants

W. T. MAYER

Engineer at San Francisco for Neilan Company, Ltd.*

WITH the continued research in the liquefaction of gas mixtures, new products which are being put into commercial use have been developed, among which are butane and propane. In the past two years these two petroleum products have come into considerable prominence as a source of fuel supply for small communities out of reach of natural gas service from a distributing pipe line. A relatively large number of butane-air mixed and straight butane gas plants have been built in all sections of the United States to supply communities ranging in population from 1000 to 25,000.

Several types of plants have been designed, some of which use a B.t.u. controller for keeping the heat value of the butane-air mixture at a constant predetermined value. Others utilize the straight butane vapor, which is further gasified by heating in a simple boiler arrangement. Another method is by proportional mixing of the butane vapor and air, which mixture is then sent out into the distribution system.

Regardless of the system used, the main objective is to obtain a gas of uniform heat, whether it be in B.t.u. per cubic foot or per pound of liquid used for generation of a cubic foot of finished gas. This means that the various refiners producing liquid butane must have absolute and accurate temperature and pressure control in their process plants in order to obtain a product that can be labeled "99 99/100% pure." In view of the careful design work done by builders of the butane-air gas plants, it is only natural to expect that the same degree of accuracy should be followed out in producing the raw material. The only way in which this can be successfully accomplished is by the installation of the proper temperature and pressure controllers in the producing plants.

DESIGN OF PLANTS

To obtain a general idea of the care that has been expected in the development and design of modern butane gas plants, let us look at the schematic drawings of a few typical installations:

In the plant shown in Figure 1, liquid butane is stored under pressure. From the storage tank (1) the butane vapor line leads through a solenoid-operated valve (2), a high pressure reducing regulator (3), a semi-high to low pressure reducing regulator (4); thence through a differential regulator (5), through the surge tank (6), solenoid valve (7), and finally to the mixing tee ahead of the compressor. An air filter and solenoid shut-off valve are provided in the air intake line leading to the mixing tee. From the compressor, the butane-air mixture is lead through a heat exchanger and thence to the finished gas storage tanks where it is stored under a maximum pressure of 75 pounds per square inch. The heat exchanger has the function of vaporizing the liquid butane by utilizing the heat of compression of the compressed butane-air mixture and also of dehydration. Electric vaporizers are provided so that vaporization may be carried on during severe cold weather.

From the finished-gas line, a sample line is led through a pressure reducing regulator to the B.t.u. controller and another reducing regulator is installed in the send-out line leading to the distribution system. The finished gas storage line and the butane vapor supply line are both

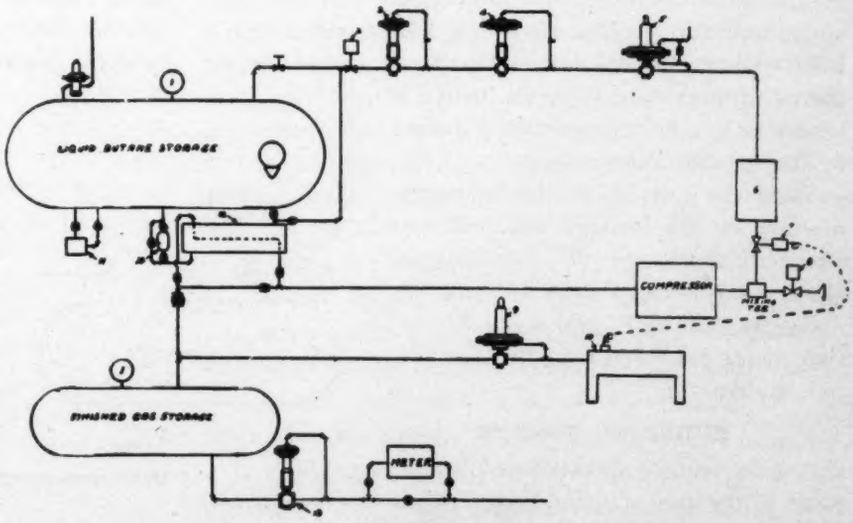


FIGURE 1

Typical modern butane gas plant with liquid butane stored under pressure

*Read at meeting of California Natural Gas Association, March 24.

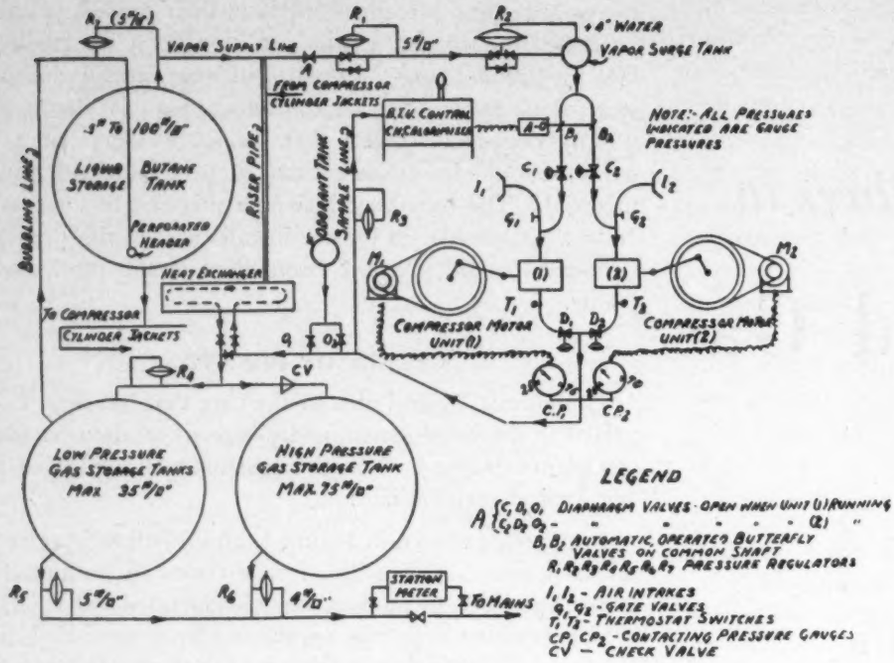

VAPOR SUPPLY LINE
VAPOR SURGE TANK
FROM COMPRESSOR CYLINDER JACKETS
B.T.U. CONTROL
A-O
NOTE:- ALL PRESSURES INDICATED ARE GAUGE PRESSURES
LIQUID BUTANE STORAGE TANK
PERFORATED HEADER
RISER PIPE
BUBBLING LINE
ODORANT TANK
SAMPLE LINE
HEAT EXCHANGER
To COMPRESSOR CYLINDER JACKETS
COMPRESSOR MOTOR UNIT(1)
COMPRESSOR MOTOR UNIT(2)
CV
LOW PRESSURE GAS STORAGE TANKS MAX. 35"/0"
HIGH PRESSURE GAS STORAGE TANK MAX. 75"/0"
STATION METER
To MAINS
LEGEND
A {C, O, O, DIAPHRAGM VALVES - OPEN WHEN UNIT (1) RUNNING
C2 O2 - " " " " (2) "
B1 B2 AUTOMATIC, OPERATED BUTTERFLY VALVES ON COMMON SHAFT
R1 R2 R3 R4 R5 R6 R7 PRESSURE REGULATORS
I1 I2 - AIR INTAKES
G1 G2 - GATE VALVES
T1 T2 - THERMOSTAT SWITCHES
CP1 CP2 - CONTACTING PRESSURE GAUGES
CV - CHECK VALVE

FIGURE 2
Flow diagram of carbureted gas production plant

protected against excessive pressure by the installation of relief valves.

The type of plant shown in Figure 2 is similar to the one just described, but has some features which improve the operating efficiency.

In normal operation, the butane is vaporized by means of the waste heat of compression and atmospheric heat. The butane vapor is led from the vapor space in the top of the liquid storage tank through reducing regulators R_1 and R_2 where the pressure is reduced in two stages; first to five pounds per square inch and then to four inches of water column pressure. From the second regulator the vapor is piped into the vapor surge tank; thence through the butterfly valves B_1 and B_2, through the diaphragm shut-off valves C_1 and C_2 to the intakes of the compressors. Normally only one compressor is in operation and so we shall deal with this single unit, No. 1. The air intake I is provided with a filter of conventional design. From the intake the air passes through gate valve G_1, which is set so as to give a proportional mixing of the air and butane vapor.

From the compressor the air-butane mixture is led through the heat exchanger; thence to the finished gas storage tanks and finally through reducing regulators R_5 and R_6 to the station meter and thence to the distribution system.

BUBBLING SYSTEM

A new feature incorporated in this plant is the use of a bubbling system. Its purpose is to permit the vaporization of the liquid butane by atmospheric heat alone. This is accomplished by allowing finished gas to bubble through the liquid butane when the vapor pressure reaches a point under five pounds per square inch. When this vapor pressure drops below five pounds, carbureted gas is admitted to the perforated header by means of regulator R_7.

A sample line is taken from the discharge side of the compressor, the gas pressure being reduced by regulator R_3. The gas sample then passes to the B.t.u. controller which automatically controls the setting of the butterfly valves, depending upon the heating value of the gas.

Ample provision has been made for complete automatic operation of the plant. Starting and stopping of the motor-driven compressors is controlled by the contacting pressure gauges CP_1 and CP_2. When the pressure in the low pressure storage tank reaches the low limit of 25 pounds, the gauge CP_1 initiates the starting operations of compressor No. 1. At the same time, a solenoid valve is energized which admits gas pressure to the diaphragm operated valves A and C_1 in the butane vapor supply line, D_1 in the compressor discharge line and O_1 in the odorant line, opening these valves. At the same time, the other parts of the plant, the B.t.u. controller and the A-O unit, are put into operation.

In case of power failure, the plant is completely shut down and will remain so until the reset mechanism has been changed by the person in charge of the plant. An shut-down is signalled to the company office through electrical signal system.

The plant shown in Figure 3 uses straight liquid butane, furnishing a butane gas having a heating value of between 3043 and 2960 B.t.u. per cubic foot, depending upon the percentage of propane mixed with it for sum-

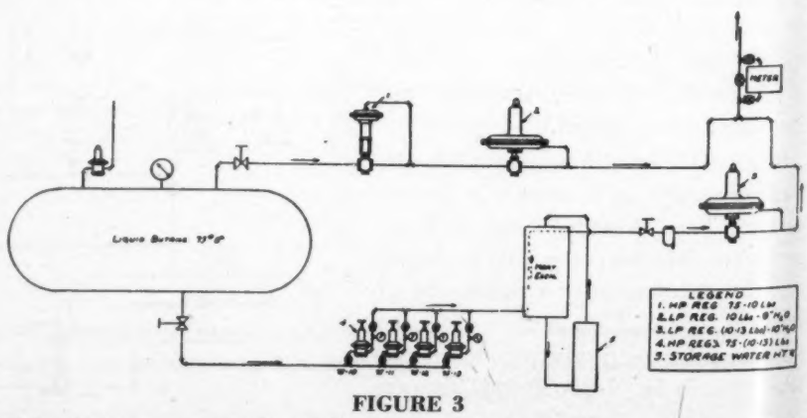


FIGURE 3
This plant uses straight liquid butane furnishing a butane gas with provision for the failure of the liquid supply

mer and winter load conditions. In the schematic drawing liquid butane is led from the bottom of the storage tank through reducing regulators (1) where the liquid is turned to gas through expansion from 75 pounds to 10 pounds. A sufficient number of regulators are used and each set at a different pressure reduction to allow for the possible freezing up of one or two and still have enough liquid supplied by the remaining regulators. The expanded vapor is then led to the heat exchanger where

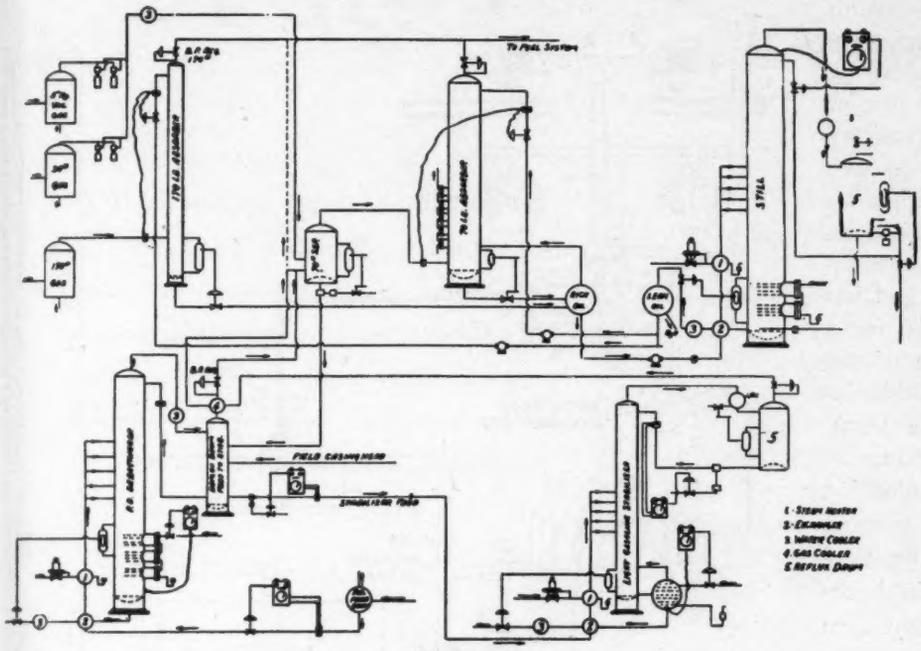


FIGURE 4
Gasoline recovery plant

it is heated to approximately 65° F. The vapor is then taken through the low pressure reducing regulator (2) and then to the distribution system under a pressure of 12 inches of water.

Provision has been made for the failure of the liquid supply. A vapor line from the top of the liquid storage tank leads through a high pressure reducing regulator (3), through a low pressure reducing regulator (2), and thence to the distribution system, under a pressure of nine inches of water. This vapor line supplies the propane vapor from the top of the liquid storage tank and is always open. However, the vapor does not always flow through due to the difference in the outlet pressures of the two low pressure regulators.

The automatic storage water heater supplies the necessary heat for raising the temperature of the expanded gas to the predetermined temperature of 65° F.

From these general descriptions, the care that has been used in butane plant design may be readily seen. Only up-to-date equipment has been used with the result that the metered gas is of uniform heating value. However, if the raw product, liquefied petroleum gas, were not of uniform quality, then even modern equipment could not produce a gas of nearly constant heating value.

With this thought of uniform quality in mind, let us turn our attention to the plant (Figure 4) that furnishes raw liquefied gas. It is interesting to note that there are an average of 21 points of control, as follows: Temperature 3, pressure 5, flow 5 and liquid level 8. Each one of these items is extremely important in the proper functioning of a stabilizing plant. Any undue irregularities in any department will have a resulting serious effect on the quality of the finished product.

CONTROL ACCURACY

Hand control in these plants is rapidly being discarded. In its place we find the most modern equipment capable of maintaining temperatures and pressures far more accurately than any system of manual control. In the past, temperature controllers that would maintain fairly constant conditions were used. However, these controllers would fluctuate within a range of plus or minus two degrees. This variation is relatively small, but is sufficiently large to make a rather decided change in the quality of the finished product.

During the past two and a half years, there has been developed a temperature controller that is a marvel of accuracy. These instruments are in service in a large number of stabilizing plants and are daily recording and controlling temperatures of less than one degree variation.

Using the principles involved in the temperature controller there also has been developed a pressure controller that gives the same high degree of accuracy.

Referring to the points of control in a stabalizing plant, we find that each has a very important function. Continually fluctuating temperatures, pressures and liquid levels easily upset the smooth operation of the units and result in poor quality products. One author has stated that "good equipment and close automatic control are essential to maximum overall efficiency and, further, smooth operation is dependent upon the sensitivity of the control instruments."

With the development of these super-sensitive instruments and the necessary control valves, there is no longer any reason why absolutely uniform operating conditions cannot be maintained. In these instruments, temperature "lag" has been practically eliminated by the use of the "thermo-pressure compensator."

The principles involved in this device are so simple that one wonders why the idea has not been translated into mechanical action long before this. Perhaps the simplicity of it is the reason. Sometimes the very simple

mechanism is overlooked and a complicated device worked out which will not function nearly as well.

The "thermo-pressure compensator" also may be called an "anticipator." In other words, the instrument anticipates what is going to happen in a process and corrects for this change before the reaction is registered on the thermal element. As an instance of this operation, let us look at Figure 5. Here we have a kettle in which a certain process is being carried out. The heating medium is steam at, say, 125 pounds gauge. Let us suppose that the temperature is to be held at 155° with an allowable variation of only one degree, plus or minus. Normally with the conventional type of temperature controller the reaction in the vessel is not registered until after the action has taken place. In this case, however, the thermo-pressure compensator has anticipated this reaction and has corrected for it. In other words, for a definite increase in the pressure of the heating medium we shall get a definite increase in temperature, and vice versa. Therefore, by controlling the pressure of the heating medium, we are controlling the resulting temperature of the process. Thus we are able to flatten out the temperature curve; hold it within the limits specified, and produce remarkably even charts as Figure 6 will show.

From another angle, let us assume Temperature "T," Pressure "P" and Composition "C" as factors. With constant temperature and pressure, the composition will remain constant. With constant pressure and increasing temperature we will get a decrease in the composition. With constant pressure and decreasing temperature we will get an increase in composition. Further, using temperature as the constant, we will get corresponding fluctuations in the composition, dependent on the pressure changes in the heating medium.

Another feature embodied is the "rota-port Synchronizer" which permits instant speeding-up or slowing down of the process rate. Merely by turning the orifice plate from one orifice to the next, the instrument may be made to increase or decrease in sensitivity. The final degree of sensitivity can be arrived at only through test.

Each orifice on the plate has the same square inch area, but they are of different shapes. In the case of the orifice for the greatest degree of sensitivity, the slightest movement of the cleaver arm will produce a definite change in the position of the control valve.

An instance of close control is given in the following facts: The desired operating temperature is 360° F. The length of the capillary tubing from the thermometer well location to the instrument is 110 feet. The control valve is 90 feet from the instrument and located in the discharge line on a turbine pump. At present this temperature recorder-controller is maintaining a temperature of less than 1° variation. This temperature is checked and recorded by a potentiometer recorder, the bulb of which is located a few inches from the bulb of the recorder controller referred to above. Obviously, such close control may be obtained only through the use of an instrument designed to do such work. In short, it is comparable to a fine watch that is rugged enough to withstand average abuse.

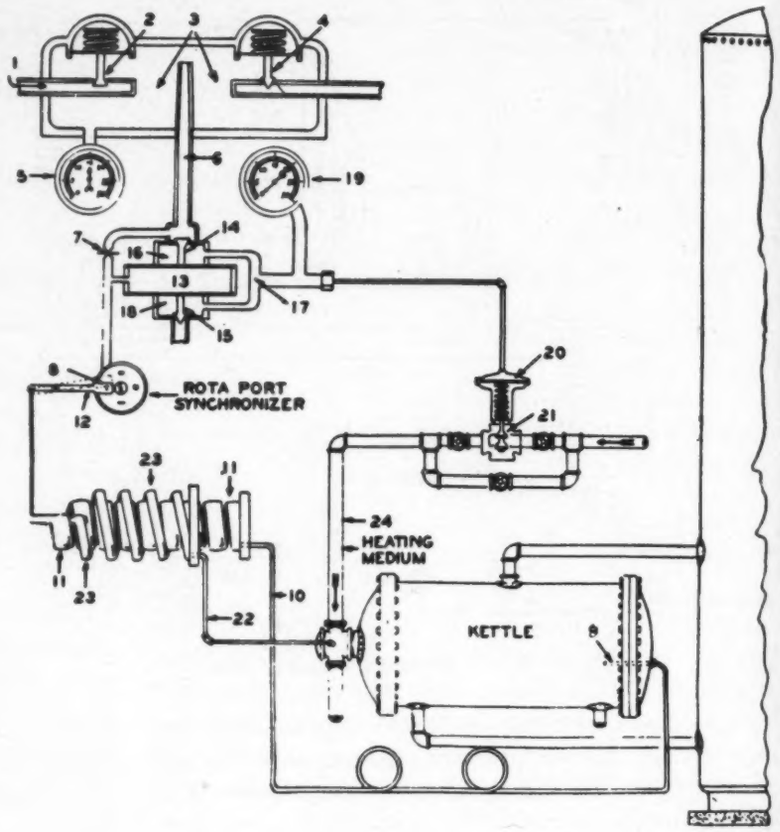


FIGURE 5

Illustrating the operation of the thermo-pressure compensator and the rota port synchronizer

A new development in a different line is that of the instrument type of liquid level controller. With the perfection of this type of liquid level controller, the oil industry is now able to maintain liquid levels with the same degree of accuracy with which temperatures and pressures are maintained. Instead of using large floats and float chambers, this new controller uses only a six-inch float. For interface or any other service where very close limits are desired, the refiner may be certain that this controller will function to his satisfaction. This is particularly true in maintaining constant liquid levels in stills, bubble towers, stabilizer towers and kettles.

Besides having the proper instrument controllers, the refiner also must have sensitive back pressure and pressure reducing regulators.

Natural Gasoline's Place • In Future Refinery Economics

EMBY KAYE

Vice President, Skelly Oil Company

THAT natural gasoline will continue to occupy a definite place in the refining industry is shown in the following address made by the author before the recent meeting of the Western Petroleum Refiners' Association, in which he discusses the commodity from its "actual value" and its "nuisance value".

IN any consideration of this subject, it is quite necessary that we recognize the fact that there is a given volume of natural gasoline production in this country, that this gasoline will be produced regardless of the immediate economics or demand, and that in one form or another it will find a market as, or in, motor fuel.

Every gallon so sold will displace a gallon of so-called refinery gasoline produced from crude oil.

This brings us squarely to the question of the place natural gasoline has in the refinery picture. It may be considered from two different aspects, (a) its actual value, and (b) its nuisance value.

Almost from the inception of the business, the natural gasoline manufacturer looked to the refiner as the natural buyer of his commodity. Even today, with all the talk that is heard on every side, the refinery is by far the largest consumer of this material.

When it is observed that the bulk of this product is being consumed by the refiner in spite of the fact that he has been effectively recovering the light ends of his own products during the last few years, one must conclude that it is either because the refiner recognizes the competitive value of natural gasoline or is able to buy it at such a price as enables him to make an out and out trading profit on the transaction.

I am inclined to believe that both factors operate at different times and that in the case of the latter it was chiefly in the extent of the natural gasoline used.

Up to comparatively recent times the refiner bought natural gasoline with two objectives. He sought to raise the gravity, and to improve the front end of his finished product.

He did such a good job of selling the importance of gravity that, as he cut deeper into his crude and later added to his gasoline supply by cracking, the refiner had to blend with his gasoline a considerable quantity of natural gasoline.

The increased gasoline yield also made for a deficiency in low boiling fractions so that during the greater part of the year refinery fuel without natural gasoline gave considerable trouble from the standpoint of starting and acceleration. Natural gasoline corrected these deficiencies and the refiner used the material as a matter of course.

Now and again, over considerable periods of time, the refiner found himself in the position of having to buy natural gasoline at the cost of painful penalties in price.

The distress prices at which natural gasoline has been marketed in the last two or three years, and particularly the price relation of this once premium product to refinery motor fuel (which itself has been sold at distress prices in the face of a continuing domestic demand right through this depression), would indicate an over-production, for one thing, or a decline in the need for natural gasoline for the erstwhile objectives, for another, or both.

The fact of the matter is that during this period (the last two to three years) production of natural gasoline declined through natural causes from something short of 7,000,000 gallons per day to 4,250,000 gallons. On the other hand, recoverable vapors from cracking units have so increased in many refineries, due to the continuous expansion in cracking facilities and recovery plants, that a large part of the shrinkage in natural gasoline has been made up right in the refinery yard.

Thus, it is entirely possible that many refineries find

themselves in position to produce a fuel with fairly suitable volatility characteristics without the use of very much, if any, outside light end products. Some of us are, no doubt, familiar with a few refiners who have an excess of light ends and who mistakenly sell this out in competition with natural gasoline, further depressing a depressed market.

The natural gasoline manufacturer saw the trend and set to work through a research program to learn more about his product. The results of this study have been too extensively published to need more than casual reference here.

OUTSTANDING ADVANTAGES

The outstanding advantages of natural gasoline over vapor recovery gasoline are (1) the very high responsiveness to Ethyl and (2) the maintenance of anti-knock characteristics over a wide range of engine operating conditions. These characteristics are of extraordinary importance when viewed in the light of recent disclosures by outstanding authorities.[1]

While the story is not yet completely written, it would appear that the refiner is going to be obligated to re-evaluate his component gasolines, particularly his cracked gasoline, with respect to its knock rating under such conditions of testing as simulate actual automobile operating conditions. Both R. C. Alden[2] and the Ethyl Gasoline Corporation have found as much as 14 octane numbers difference on certain gasolines when the tests were conducted with engine jacket temperatures of 350 to 362 degrees and 900 r.p.m., as against the current testing method.

The full extent and significance of these disclosures can be discovered by reference to Alden's Figure 3 in the article hereinbefore indicated. The stability of the anti-knocking property of natural gasoline is clearly demonstrated.

In tests conducted in our laboratories, we found similar results when we blended straight-run gasoline with vapor recovery gasoline and compared the octane stability with a blend of natural gasoline of substantially the same volatility[3]. Eighty per cent of a 50 octane straight-run gasoline was used in both cases.

	Engine Jacket Temperatures	Octane Number
(1) Natural	212°F.	55.8
gasoline	362°F.	54.7
blend	Difference	1.1
(2) Vapor	212°F.	59.8
recovery	362°F.	56.5
blend	Difference	3.3

It has been stated that the important reason for this lowering in octane rating at the higher engine temperatures is accounted for by the fact that "most hydrocarbons of the benzenoid and unsaturated type (present in cracked stock) lose their anti-knock value more rapidly at high temperatures than do the saturated hydrocarbons in straight-run gasolines."[4] This latter obviously includes natural gasoline.

Figure 2 of Alden's paper demonstrates the high responsiveness of natural gasoline to lead tetra ethyl. It shows that cracked gasolines are less responsive to lead than either natural or straight-run gasoline.

It appears that by the use of substantial percentages of natural gasoline savings in lead requirements, up to 1 c.c. (and even higher) may be made, depending upon the character of the refinery materials and the grade of natural selected. In many refineries, due to limitations fixed by the type and extent of cracking facilities, the use of natural gasoline alone has made possible the marketing of the 57-64 grade of motor fuel.

With the uncertain situation both as to ultimate requirements and methods of testing, many refineries will "sit tight" and use naturals to meet what might be a temporary competitive situation instead of joining the mad rush to make further capital expenditures to meet competition not justified by economics or automotive requirements.

It should be noted that the direct relationship that exists between octane number and Reid vapor pressure indicates further savings in tetra ethyl lead requirements as we increase the vapor pressure of our motor fuels. As fuel systems are improved—and they are being improved—there will be no valid objection to conserving those highly valuable butanes now being wasted.

Vapor lock has been demonstrated to be more a matter of fuel system design than a properly built fuel, and with the elimination of the deficient fuel system the higher vapor pressure gasolines will permit the use of larger percentages of natural gasoline with resultant decreased lead requirements, hence lower costs.

While large volumes of available natural gasoline will be used by the refiner on account of its demonstrated anti-knock value, a substantial percentage of the production will continue to flow to the refinery or its own outlets because of its volatility characteristics and high gravity.

Even though, as hereinbefore stated, some refineries have dispensed with the use of natural gasoline, surveys of competitive gasoline by several laboratories indicate that while the gasolines meet U. S. Motor specifications, few of them would fail to have their 10 per cent to 50 per cent points improved by the addition of natural gasoline.

In some states marketers still compete on gravity specifications, and, during summer and winter alike, a considerable volume of natural is used for the sole pur-

---

1Ethyl Gasoline Corp.: Correlation of Knock Testing Engine Results with Knocking in Automobile Engines, Feb. 5, 1932.

2Octane Number and Reid Vapor Pressure Relationship in Natural Gasolines by R. C. Alden, published in the National Petroleum News, Jan. 20, 1932.

3Vapor pressure of vapor recovery gasoline was 28 to 29 pounds.

4Ethyl Gasoline Report ibid.

pose of raising the gravity of motor fuel marketed in those states.

Manifestly, the refiner must recognize a certain set of facts and/or circumstances.

1. Natural gasoline is produced from casinghead gas that cannot be conserved. It must be produced from day to day. It is produced regardless of price since the manufacturer has to pay for the raw material whether the gas is utilized or not. Enormous investments have been made in plants which cannot very well be abandoned.

In addition to gasoline produced from casinghead gas, an increasing supply of gasoline is being produced from natural gas transportation systems. This gasoline is also produced regardless of returns.

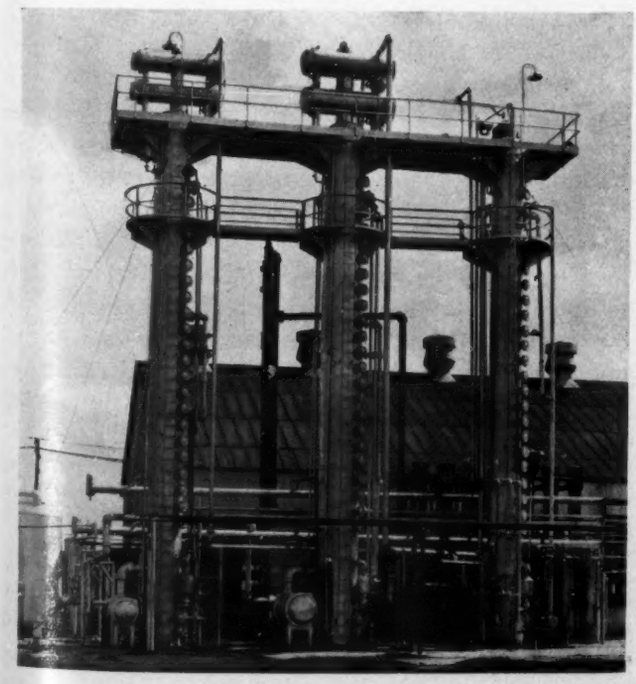
It is produced practically entirely for the purpose of purifying the gas and removing such water and gasoline as may cause interruption in service due to blocking the lines with liquids, or ice formations. Comparatively little storage is available for this gasoline. Storage for natural gasoline, as such, is expensive.

2. During the past few years, and increasingly from day to day, gasoline plants have been equipped with facilities to produce natural gasolines of subnormal vapor pressures and are, in fact, producing and marketing straight natural motor fuels with vapor pressures as low as 6½ pounds. A substantial volume of 6½ to 13-pound material moves as aviation gasoline, but a greater percentage is sold as premium motor fuels, particularly during the winter.

Many jobbers in the northern territory have featured 66 to 74 gravity gasolines for winter use and have obtained premiums of 2 to 3 cents over the 57-64 octane grade at their pumps.

3. Considerable quantities of 11 to 18-pound gasoline moved to jobbers this past winter as material to be blended with ordinary refinery gasoline. The blends of 64 to 66 gravity attracted considerable consumer interest. The consumer liked the starting qualities of the high gravity blend. The addition of the excess of, say 67 to 70, octane natural of 12 to 14 pounds did not hurt the anti-knock quality of the fuel.

[5]Issue of March 17, 1932.



4. The availability of cheap natural gasoline has been an outstanding contributor to the low prices that have obtained for motor fuel. The price cutter does not fail to see the merits of natural gasoline.

Why should he not buy an 11-pound natural, a gasoline of superior quality with an octane number of 66, when he can obtain it at from 1½ to 2 cents less than he would have to pay for a medium octane grade of refinery gasoline?

He is in position to sell this product for less than the regular marketer must obtain for his standard product. And this is exactly what has happened and is happening today.

Moreover, when 26-70 natural gasoline sells at a substantial differential under refinery gasoline, this price cutter can make his own blend and still undersell his competitors.

Now I do not mean to imply that all jobbers who buy naturals of one sort or another, when a price differential obtains as against refinery gasoline, are price cutters.

Some jobbers—indeed, a great many—simply save the difference, and others use naturals because they recognize the selling power of an especially blended product which they feature, often at a premium.

They are in an especially favorable position to blend instanter to meet local atmospheric conditions, and can in this way gain considerable consumer favor.

5. It has been estimated by C. O. Willson in the Oil & Gas Journal[5] that there is being produced in the Mid-Continent at present 300 cars of natural gasoline and 1250 cars of refinery gasoline per day. The 1250 figure contains possibly from 75 to 100 cars of natural gasoline, leaving approximately 200 cars which must be absorbed by the decreasing export trade or by refiners and distributors through the refinery or through refinery-owned bulk stations or independent jobbers.

It is these 200 cars of natural gasoline, part of which are now moving to recognized markets, which must be absorbed in preference to gasoline from crude oil. This is the gasoline that has looked for a market and found it—at distress prices—to the detriment of the whole refinery price structure.

No informed refiners need be told through this medium that natural gasoline is being sold at these ridiculous prices (measured against refinery gasoline prices) by some of the largest oil companies in the business, when so many of them could, if they would, reduce runs and absorb the excess natural gasoline.

6. The natural gasoline group has been forced to develop technical and mechanical data on blending and intends to make the information available to jobbers and dealers. No doubt it plans a publicity campaign to

further the sale of its superior products in direct competition with refiners.

You must admit that with a price advantage which it can offer along with the superiority of its products, as discussed herein, the time may have arrived when success would attend its efforts.

The gasoline group is ably manned and has given a good account of itself in mechanical and technical development, and I vouchsafe it will fight its way out of the economic dilemma, in which it now finds itself, if forced to do so, by a large-scale cultivation of direct marketing outlets. This step might be expensive, and will be used only as a last resort.

If, then, we face these facts and circumstances, it is clearly indicated that, to protect his markets and price structure, the refiner should absorb either through the refinery or bulk station such natural gasoline as is available today, of whatever specifications he desires, at a fair price in relation to the middle grade of motor fuel.

It has been suggested that a fair price for 26-70 would be 85 per cent of the price of motor fuel, with an 11 to 15 per cent differential for each grade lower than 26-70.

The refiner need have no fear of the skyrocketing affect of concerted buying upon prices. The gasoline manufacturer has learned a good deal of late on this score, to his regret. The wide fluctuation in prices with its accompanying fluctuation in demand made for a feast or a famine.

The manufacturer now looks with favor upon contracting his output at a differential based on the motor fuel price. When this idea was first proposed[6], it met with strenuous opposition from the manufacturers group, but it is today recognized as eminently fair.

With properly equipped storage, a perfectly homogeneous blend of natural gasoline and refinery products can be made at the bulk station if the refiner-distributor desires to save a substantial part of the in and out freight. The refiner can thus usually make a profit on the turnover. It does not require any particular genius to make a blend that will in every respect duplicate the refinery-blended product.

It is particularly to the refiner's advantage to ship partially debutanized or butane free natural gasoline to his bulk station for blending, as against using any natural gasoline in his refinery. In other words, instead of paying an in and out freight on natural gasoline, he can use the freight saving to pay a premium for the more stable natural gasoline.

What to do about natural gasoline is our problem as much as it is that of the natural gasoline manufacturer. It is begging the question to debate the merits of the product. The refiner can and should provide an outlet for this material. This problem—your problem and my problem—will not be solved by what we say here, but by what you and I are going to do about it.

[6]H. B. Bernard, Sinclair Oil & Gas Co., at A. P. I. meeting in California, 1925.

SELECTION *of* Cracking Involves Analysis

SELECTION of a stock for cracking purposes is much more complicated and difficult than is the selection of crudes for topping operations. The value of a crude for skimming or topping can definitely be established by laboratory determinations. The quantity and quality of the gasoline, the kerosene, the gas oil, and the fuel oil that can be made from a crude can be accurately predicted before actual plant operation is begun.

The products from a cracking plant, however, are so dependent on the conditions of temperature, time, feed stock, etc., that entirely different products and yields are obtained depending on the varying of certain of the conditions. However, the selection of charging stocks for cracking plants can be made by an intelligent consideration of the following factors, coupled with the correct application of a certain stock to its best type of cracking conditions. The most important factors in the order of their probable importance are:

1. Distillation range.
2. Carbon residue or tar number.
3. Aniline number.

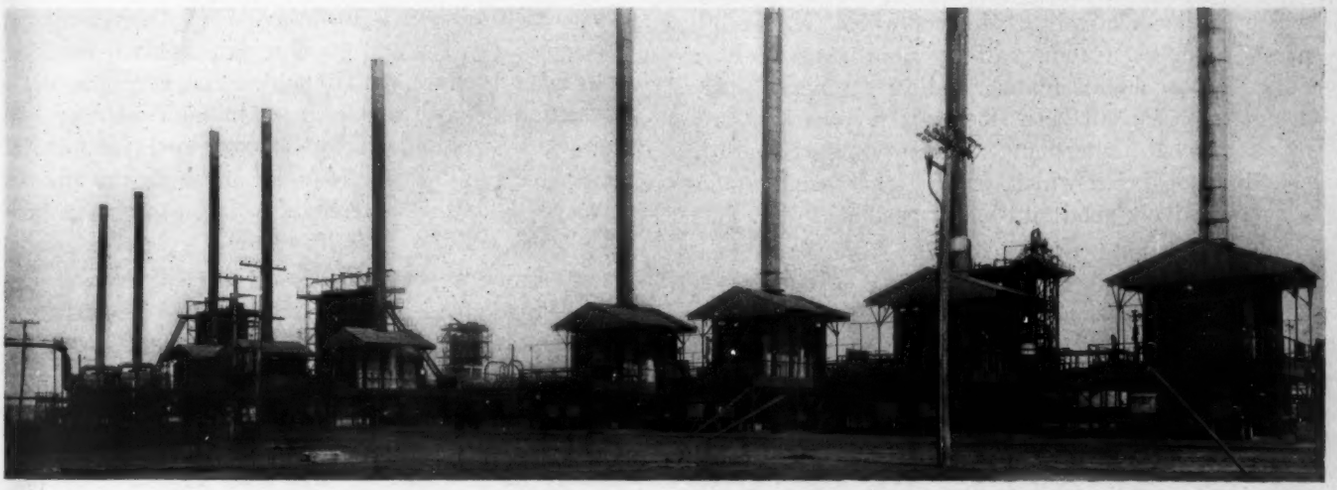
Sachaven and Tilicheyev have shown that the rate of cracking is a function of the boiling range of the cracking stock. Light gas oil takes nearly twice as long to crack as heavy fuel oil, and kerosene is five times as slow as the gas oil. The more closely fractionated the cracking stock, the more efficient is the cracking. It is obvious that a crude oil which contains 15 per cent virgin gasoline, 10 per cent kerosene, 60 per cent gas oil and 15 per cent asphalt can not be cracked efficiently. The high temperature required to crack the gas oil will overcrack the asphalt, thus increasing the coke formation, and the comparatively lower temperature required to crack the asphalt will leave the gasoline practically unaffected.

One system, which is incorporated in the most modern cracking units, is to flash the natural gasoline by means of preheaters, and to remove the asphalts and heavy hydrocarbons rich in coke-forming compounds

Stocks Accurate

A. W. TRUSTY

Chief Chemist, Louisiana Oil Refining Corporation



Nine Cracking Units at the Bossier City, Louisiana, Plant of Louisiana Oil Refining Corporation.

with the fuel oil, and thus neither the lightest nor the heaviest hydrocarbons actually reach the cracking coils. An example of a feed stock which has been stripped in the above manner is given:

	Cold Fresh Feed	Hot Feed to Cracking Coil
Gravity	25.3	23.2
I. B. P.	240	410
10 per cent at	406	480
20	506	512
30	578	533
40	605	550
50 per cent at	650	568
60		574
70		623
80		660
90		...
Carbon Residue	2.50%	0.16%
Tar Number	36	8
Flash	105°F.	210°F.
Fire	160°F.	245°F.
Color	Black	Translucent

The carbon residue test is made as described in U. S. Government Bulletin 323-B. The tar number test is made as follows:

In a 100 c.c. glass stoppered cylinder put 100 c.c. of the oil to be tested and add 10 c.c. of 66 Baume sulphuric acid. Shake for two minutes and allow to stand for 1½ hours. Read the volume of tar substract 10 c.c. for the volume of acid added and report the result as the tar number. For heavy crudes and residues it is necessary to use 50 c.c. of kerosene and 50 c.c. of the oil to be tested, in which case the volume of tar is doubled (after being corrected for the volume of acid added). The tar numbers on some stocks are shown:

Kerosene . . . . . 0 Tar Number
Cracked straw G.O., 32 Gravity . . . 2-4
East Texas Crude, 39 Gravity 16
Smackover Crude, 22 Gravity 60
Fuel Oil, 14 Gravity 100

The tar number is a rough indication of the amount of tar or carbon forming compounds present in the feed stock. The lower the tar number can be maintained on the cracking coil feed, the lower will be the coke formation, other factors being equal.

The carbon residue and the tar number have a rough relationship to each other. The carbon residue is the more accurate of the two; however, the test is longer and requires the time of a chemist to make the test, while the tar number test can be made in a short time by a routine tester. The tar number is an excellent test for plant control when operating on the same crude stocks over a long period. However, when operating on a varying mixture of paraffin and asphalt base crudes, the tar number is subject to variations. A combination of the two tests, checked periodically, gives a good routine feed stock control.

ANILINE NUMBER

The aniline number is the temperature at which equal volumes of oil and pure aniline are miscible. The test

is made by adding to a test tube 10 c.c. of freshly distilled aniline and 10 c.c. of the dry oil to be tested. Insert a thermometer and a wire stirrer. Place the test tube in a larger test tube filled with water. Heat slowly with constant stirring and record the temperature at which the two compounds make a clear solution.

The paraffin hydrocarbons are miscible at about 170-185°F., the naphthenic hydrocarbons at about 150 to 160°F., the unsaturated hydrocarbons somewhat lower, and the aromatic hydrocarbons are miscible at all normal temperatures. Aniline numbers on some typical stocks:

Mid-Continent straight-run gas oil—33 grav.... 169°F.
East Texas straight-run gas oil— 33 grav.... 180°F.
Cracked gas oil (Recycle G.O.)— 32 grav.... 110°F.
Straight-run gas oil from Smackover Crude— 29 grav.... 144°F.

A high aniline number indicates a paraffin base stock, which cracks relatively easily, but which, on the other hand, produces a comparatively poor anti-knock gasoline. A low aniline number indicates a naphthenic or aromatic or asphalt base stock which must be cracked at a somewhat higher temperature to produce the corresponding yield, but which, on the other hand produces a comparatively good anti-knock gasoline.

In the cracking of a paraffin stock, symmetrical cracking of the molecule with no coke is the result. Of course, coke is formed at high temperatures, but this is due to secondary cracking, or cracking of products formed in the cracking of the paraffins. As the temperatures rise or as secondary reactions come into play, olefins increase up to a certain point, as does methane, hydrogen steadily increases, diolefins begin to form, then aromatics and finally coke.

As far as pure paraffins are concerned, no tar and coke are formed by moderate cracking. The naphthenes, which are hydrogenated aromatics, dehydrogenate to form aromatics, and these lose more hydrogen, condense and coke forms. Aromatic charging stocks are considered the most refractory, both from the standpoint of ease of cracking and amount of gasoline formed, and are also greater coke formers than other stocks.

In the cracking process the coke is formed mainly from aromatic hydrocarbons which are primarily condensed during the cracking according to the scheme: benzene C_6H_6, diphenyl $(C_6H_7)_2$, naphthalene $C_{10}H_8$, dinaphthyl $C_{10}H_7$, etc., or, as is noted there is a constand splitting off of hydrogen. On further cracking, the newly formed high boiling aromatic hydrocarbons are subjected to a further condensation, forming heavy tar-like products which are finally converted into coke.

Therefore, if cracked gasoline is the product of the primary destruction of high molecular weight hydrocarbons, coke is the last stage of a number of consecutive condensation reactions. Therefore, cracked gasoline is formed during the first stage of cracking of the greater majority of crude oil products, while no coke is formed; simultaneously an accumulation of heavier condensation products takes place in the cracked residue. As soon as the yield in cracked gasoline reaches a certain magnitude, the formation of coke sets in, increasing rapidly in the course of cracking.

RECYCLING

Only a limited amount of gasoline can be formed in a single cracking step if coke formation is to be avoided. A large portion of the original charging stock will remain in the form of intermediate oils, which cannot be cracked further without at the same time degenerating part of the tar into coke. Less cracking per cycle can be permitted on stocks of high carbon-hydrogen ratio, such as topped crudes, than on light gas oils if excessive coke formation is to be avoided. The continuous removal of tar, gas and gasoline as produced, would be an ideal procedure, and would entirely eliminate the production of coke and result in a high yield of light products. An approach to the continuous removal of the products of cracking is found in the present practice of recycling, with the removal of tar, gas and gasoline after every cyle.

Laboratory experiments made by Sydnor and Patterson, Standard Oil Company of New Jersey, show the effect of recycling on the cracking yield and aniline number of a gas oil.

	Aniline No.	Gaso. Yield
Pass 1—Straight-run Mid-Continent Gas Oil	169°F.	24.3
Pass 2—Recycle gas oil from Pass 1	142	19.3
Pass 3—Recycle gas oil from Pass 2	126	16.7
Pass 4—Recycle gas oil from Pass 3	106	14.9
Recycle gas oil from Pass 4	84	...

The conclusions made on the recycling of a cracking stock were:

(1) The yield of gasoline on the feed stock to each pass decreases.

(2) The ratio of fuel oil yield to gasoline yield increases.

(3) The A. P. I. Gravity corresponding to a given boiling range is lowered.

(4) The boiling range of the gas oil produced is lowered.

(5) A decided change in the chemical composition of the recycle gas oil occurs, as indicated by a decrease in the aniline number.

CONCLUSION

The ideal cracking stock is a heavy, closely fractionated gas oil fraction with a low carbon residue, low tar number, and low aniline number.

USE *of* LIME *in the* Petroleum Refinery

SIDNEY P. ARMSBY
Chemical Engineer

PART 2

IN this, the second of a series of articles dealing with utilization of lime by petroleum refineries, Sidney P. Armsby outlines the various types of modern equipment employed for handling and distributing the chemical. There is a great deal of difference between limes; chemically hydrated lime for grease manufacture, a quick-lime for water softening, a specified grade of hydrate for combatting corrosion, a by-product lime for neutralizing acid sludges, a quicklime for naphtha treating or a masons' hydrate for construction work. The writer discusses the characteristics of the various grades, proper methods of handling, storing and distributing each, and their proper field of application in the refinery, and a portion of this article is given over to discussion of proper safety devices and measures required for handling this chemical.

The third article, to appear later, will outline the uses of lime in refining operations taking five grades and applying them to proper departments, and include discussion of use of lime for preventing corrosion in tube stills for crude oil, cracking stills, and its utilization in treating various distillates and gases, and in water softening, neutralization of acid sludge, construction and sanitation work.

BEFORE endeavoring to decide how lime should be handled in any refinery, careful consideration should be given to all factors governing its use in the various departments it is to serve. Failure to observe this simple precaution is certain to involve unnecessary expense and result in endless trouble, until mistakes have been rectified.

Fundamental considerations, which will determine lime handling methods and the choice of mechanical equipment, are:

A—Character of the lime as received.

B—Whether to be used in same form as received.

C—Processes to be served.

D—The Time Element—whether to be used up quickly, slowly, continuously or intermittently.

E—Quantity to be used per day in each separate department.

F—Labor cost involved in handling.

G—The Human Element—safety and comfort of men engage inhandling the lime.

Taking up these various fundamentals in the order listed, we will endeavor to develop a set of working principles that may serve as a guide in planning an economical lime-handling layout, capable of caring for the requirements of any oil refinery—large or small.

(A) Character of the Lime.

Under this heading we must consider both the chemical and physical characteristics of the lime as it is received at the unloading point: whether it is quicklime or hydrated lime; in large lumps, small lumps or powder form; quick-slaking or slow-slaking; in bags, barrels, steel drums or in bulk; containing large or small amounts of core; a highly purified product or one of relatively low grade; and so on, through all the features which distinguish one type or grade of lime from another. As shown in part one of this series (What Constitutes a Good Lime, Ref. & N. G. M., Vol. 11, No. 4, 1932, page 291) it may be found desirable to procure various types or grades of lime in order to secure the greatest process efficiency throughout the refinery. It is equally important to provide the most efficient handling system for each grade of lime, if we expect to maintain that plant efficiency. In some cases, different methods of handling may be required for each lime purchased, while under other conditions the same equipment may be used at alternating periods for two or more different materials.

There is a vast difference, for example, between a chemical hydrated lime especially prepared for grease making and a quick-lime intended for water softening. Or between a specified grade of hydrate for treating charging stock and a by-product lime for neutralizing waste acids, or between a quicklime for naphtha treating and a masons hydrate for miscellaneous construction work.

In the first example cited, the grease-making lime needs only to be removed from the car and transported to a suitable storage room in the grease plant, near the point of application and where it will be adequately protected against deterioration or contamination. Such a lime will probably be received in strong, well-made bags which afford easy handling by hand truck, elevator or mechanical conveyors, and also protect the lime against air-slaking. Its handling involves the simplest of mechanical equipment and, if only that one type of lime were used in the refinery, the entire handling problem could be solved by any good mechanic. With the quicklime for use

in water softening, however, the problem becomes more complicated, and must be given very careful study. This material will probably be received in bulk, in box cars, and the first thing to be done is to get it out of the car and put it where it will be ready for use. If it contains large lumps, the cargo can be unloaded by the use of wheeled scoop-trucks and man-power. It may, however, be much more economically (and comfortably) handled by means of a power shovel, actuated by a winch set up along side the track and operating through two sheaves fastened to either side of the car door frame. The cable is slipped into either sheave as desired and the operation of the winch is controlled by the man operating the shovel inside the car. This allows all corners to be easily reached and the lime to be scraped over to the door, to fall into a hopper provided for the purpose, close along side and just below the level of the car floor. This hopper would feed a bucket elevator or cleated belt conveyor which would deliver the lime to storage bins, slaking tanks or crushing equipment. If, on the other hand, the largest pieces of quicklime are of sufficiently small size, then the whole job of unloading and transporting to the next handling stage can be done quickly, easily and efficiently by means of any one of several standard makes of air conveying equipment now on the market, and in general use for both loading and unloading of grain and other products. Such installations have already been applied to the handling of bulk quicklime, and full engineering details are readily available. An unloading system of this type possess the advantages of large capacity, saving of space and freedom from dust—in addition to which it can usually be operated by one man.

HANDLING BY-PRODUCT LIME

In the second comparison mentioned above (treating charging stock and waste acids) this first, or unloading, step presents considerations similar to those just discussed—the by-product lime probably being best handled out of the car by an air-conveying system. (Indeed the same air conveyor could probably be used to handle both this and the quicklime mentioned above, merely by providing for delivery to two separate storage bins.)

Again, in the third illustration, the same general principles might be utilized for handling the quicklime on its way to the naphtha treating process, while the masons hydrate, received in convenient bags, would probably be stored in the warehouse. It is the subsequent steps in the journey that call for further study of handling methods.

(B) Form in which Lime is Used.

In the grease plant hydrated lime is generally used "as is", being taken from the sack and added directly to the other ingredients in the mixing kettle. Obviously, a minimum of equipment is required to bring lime from the storeroom to the kettle, and a sharp knife will serve for opening the bags as required. Thus the fact that the lime is used in the same form in which it is received insures its being handled most economically with the least possible mechanical equipment and with a minimum power consumption.

PREVENTING CORROSION

But if this same hydrated lime is to be used for preventing corrosion in still tubes, the picture looks very different. In this case provision must be made; first, for thoroughly mixing a pre-determined weight of lime with a definite volume of oil as a carrier, and second, for the introduction of a certain definite dosage of the lime-oil mixture into the stream of crude oil entering the still. Only by some such accurate system of proportioning can the correct dosage of lime be maintained within the still tubes. The lime-oil slurry may be made up by the batch process, in which two mixing tanks are used in series—a fresh batch of lime and oil being mixed in one tank while the previously prepared batch is being drawn out of the other tank. Or it may be made up continuously by using a chemical dry-feed machine which can be regulated so as to discharge a given amount of lime per minute into a stream of oil which is next suitably agitated, to disperse the lime, and then injected into the main stream entering the still. The choice of methods for preparing slurry will be governed by considerations of quantities, labor costs and other factors, but it is necessary to plan correctly for handling the lime after it has been unloaded and delivered to the distillation department, and it is essential to provide means for accurate control of the dosage of lime entering the stills.

At the Smith's Bluff refinery of The Pure Oil Company this problem is taken care of easily and economically as described by R. J. Lawrence, resident chemist, in an earlier issue of this magazine. (See The Refiner and Natural Gasoline Manufacturer for August, 1930.) We quote in part from that article, as follows:

> "The method of operating this plant is to fill one of the two vertical open-top tanks with 20 barrels of the charging stock which is being charged to the stills. Into this tank, by means of a hopper and a small bucket elevator, 18 40-pound sacks of hydrated lime are dumped, giving a mixture that delivers to the stills 0.4 pound of lime per barrel of charging stock. This is thoroughly mixed with the oil by a rotating stirrer turned by a small motor; this mixer stirring the oil and lime continually throughout the pumping out of each batch. An air connection is placed in the bottom of the tanks so that in case of electrical or mechanical trouble the operator can continue to agitate the oil and lime. One batch is used up in about one and one-half hours and, while pulling from one tank, a batch in the other tank is in preparation.
>
> "From the mixing tanks the lime and oil are passed

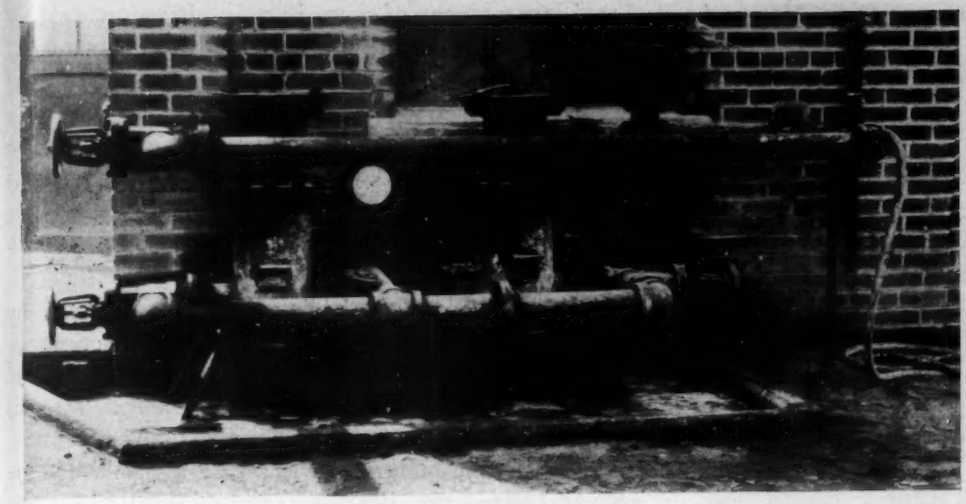


FIGURE 4

The lime-oil mixture leaving the mixer, passes through a set of screens and into the suction of the delivery pump.

through a set of 14-mesh screens and into the suction of a small steam pump. From this pump it is discharged into a three-inch line, running the full length of the stills, the excess oil returning through a two-inch line into the bottom of the tank, completing the cycle. This circulating line insures a uniform mixture being delivered to each still. From off the three-inch line and directly behind each still, a one-inch line is run into each control house.

"This line carries the oil and lime to a small plunger pump; the speed of the stroke of this pump being the same as the stroke of the still's charging pump, as the plunger rod of the lime pump is clamped to the piston rod of the charging pump. This small lime pump operates with a full stroke at all times, the amount of lime charged to the stills being controlled entirely by the mixture in the lime-mixing tanks.

"On the side of the line feeding the lime pump is a gauge glass which indicates to the operator whether or not the mixture is feeding to his pump. At intervals the operator opens a valve on a small line on the discharge of the lime pump to be doubly sure he is getting lime into his still."

Figures 4 and 5 show two of the essential elements of this simple and easily-controlled installation.

Hydrated Lime and Water. Equipment similar to that illustrated above may be used for making up and applying suspensions of hydrated lime in water. Such milk-of-lime treatment is in general use at industrial and municipal water treating plants throughout the country and needs no elaboration here. Suffice it to say that the same method of controlling the dosage of commercial hydrated lime may easily be practiced when the lime is used for such operations as removing hydrogen sulphide from naphtha; neutralizing excess acids; preventing corrosion in condensers, and for many other purposes.

SLAKING QUICKLIME

Slaking of quicklime is probably the most important phase of the lime-handling problem in any oil refinery using lime in appreciable quantities. Failure to provide economical means of correctly slaking the bulk quicklime received has caused, and will continue to cause, inefficient use of the lime and extra expense that is entirely preventable. The remedy is very simple—correctly designed and efficiently operated slaking equipment, including the feeding of quicklime to the slaker and the removal of the material discharged from it. The slaking of quicklime is, in reality, a distinct chemical process operation by which the calcium oxide content of the lime is converted into calcium hydroxide, and it becomes a part of the oil refiner's lime-handling problem simply be-

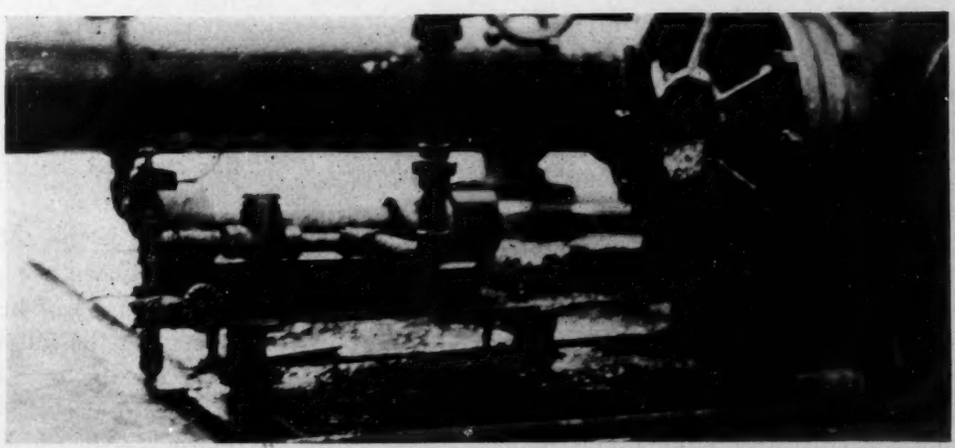


FIGURE 5

The plunger of the lime pump is clamped to the plunger of the crude oil pump, thus synchronizing the lime dosage.

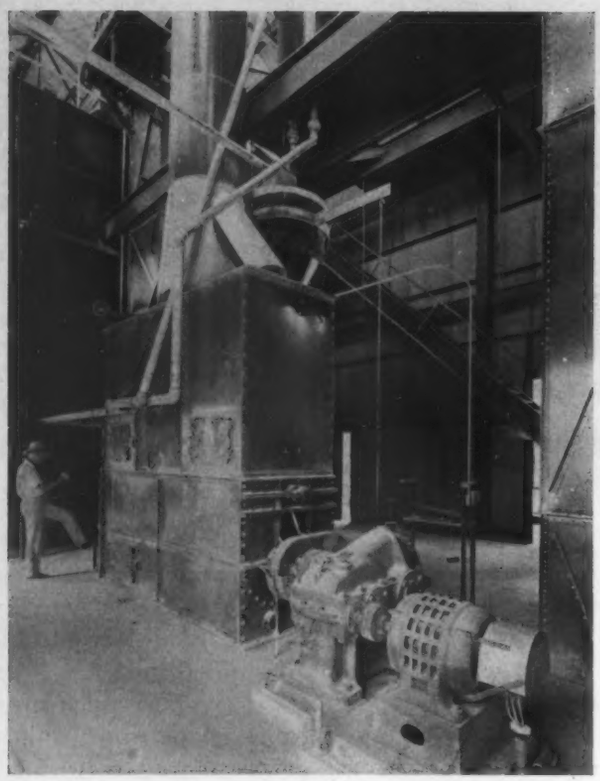


FIGURE 6

Batch-type lime hydrator with automatic weighing hopper for quick-lime and measuring tank for water. Motor in foreground drives the agitator.

cause he wishes to procure more active calcium oxide for each dollar spent—adding the water to it himself instead of buying and paying freight on this water in the form of hydrated lime.

This is a logical procedure if properly executed. But if improper slaking methods cause a watse of 20 per cent of the available calcium oxide (as has been known to occur) and excessive power, labor and time costs add a burden equivalent to another 10 per cent, then all the advantages of a cheap unit cost have been wiped out, leaving in their stead an item for depreciation of equipment.

STUDY REQUIRED

In view of the fact that the oil refiner must always convert his quicklime into hydrated lime before he can use it, and the further fact that no two brands of quicklime react in exactly the same way when treated with water, the writer again urges upon both oil refiners and lime manufacturers a closer co-operation in the interests of process efficiency. Many lime producers have developed detailed technical data regarding the slaking properties of their respective quicklimes, and are in position to furnish accurate information as to the correct practice to be followed in order to secure the best possible efficiency when using them.

POSSIBLE INSTALLATIONS

(1) Instead of trying to slake a quicklime consisting principally of large lumps, or containing occasional large pieces of core, in a cumbersome system of large tanks, with periodic shut-downs for removal of accumulated core and sediment, it may be found more economical to first crush the lime down to a certain maximum size. A saving in size of tanks or amount of agitation required; a more perfect utilization of available lime, or an easier method of removing core (such as screening in transit) may more than pay the crushing cost.

(2) A small-lump quicklime can be delivered by an air conveyor directly into a continuous type of lime slaker which will discharge a uniform flow of milk-of-lime, carrying the impurities along with it at a constant rate instead of allowing them to accumulate at any one point. (In this case the milk-of-lime may be passed through a rotary or vibrating screen to remove the impurities or, if they are inert in the process to which the lime is going, they may be allowed to flow along with it.)

(3) It might be desirable to convert quicklime into a lime-oil slurry, such as was discussed above under that heading. It is easily possible to install hydrating machinery, similar to that used in lime plants, which will convert the quicklime into a dry hydrate. This hydrate could be discharged into lime-oil mixing tanks and the evenly distributed impurities either screened out of the slurry or allowed to remain, according to process requirements.

(4) It is possible that slaking equipment adequate for handling a slow-slaking lime will be found unsatisfactory for a quick-slaking one, and mechanical changes will be required to make the installation function properly.

All these, as well as many other important problems can be solved more easily by the oil refiner if he will call the lime manufacturer into consultation, and both industries will profit by the exchange of ideas. The lime will give more efficient service, and the refiner's process equipment will be simplified and his costs reduced.

(*C*) *Processes to be Served.*

Under this heading we will deal principally with questions of inter-plant transportation, handling and storage as these are affected by the use that is to be made of the lime, and without regard to the relative importance of each use—these points being covered in later paragraphs. Two hypothetical cases will serve to illustrate the considerations necessary at this stage of the development of plans for a lime-handling system.

(1) Suppose the only available unloading point is midway between the grease plant and a warehouse used for storage of building materials, and that we are receiving the following grades of lime: chemical hydrate for the grease plant; mason's hydrate for construction purposes, and quicklime in large lumps to be used in the form of lime-oil slurry for a battery

of tube stills. The most economical system of handling in this case probably would line up about as follows: First, either trucking or mechanical conveying of the two grades of hydrated lime to their respective places of storage. Second, quicklime equipment composed of the following items; (1) a power shovel for emptying the car, (2) a receiving hopper along side and below the car floor, (3) a lime crusher set below and fed by the hopper, (4) an enclosed bucket elevator fed by this hopper ,(5) a hopper-bottom storage bin filled by the bucket elevator, (6) a lime hydrator (batch or continuous) served by gravity from the storage bin, (7) a supply of crude oil from some nearby line, (8) a lime-oil mixer (batch or continuous) fed by gravity from the hydrator, (9) screens for removing core and impurities from the slurry, (10) an extra agitator tank to hold an emergency supply of slurry, (11) pump, pipe line and distributing system to the stills. With these eleven items compactly built and properly co-ordinated, the only manual labor required for handling the quicklime up to the point of consumption will be one man for the power shovel and one man for operation of machinery. The still foreman will have his lime delivered to him by the most economical method and in the most convenient form for instant use.

(2) To vary the discussion, let us assume the purchase of chemical hydrate for the cracking stills and a small-lump quicklime, containing little or no core, which is to be divided between water softening and the treatment of acid waste. Also assume available space for lime-handling equipment close to the unloading point. Under these conditions the simplest layout would consist of two separate units in the same building, as follows: First, a suitable mechanical elevating system to deliver the sacked hydrate to a storage room (on the upper floor of the building) located to serve a lime-oil mixer through a feed hopper or mechanical feeder, the mixer being followed by a pump and pipe line distributing system to the stills, as outlined above. Second; an air conveyor would unload the quicklime and deliver it to an overhead storage tank, having a hopper bottom and discharging by gravity into the feeding mechanism of a continuously operating lime slaker. The stream of milk-of-lime leaving the slaker would be handled by pipe lines and pumps serving both the water-treating and acid-treating plants — suitable emergency storage tanks, with agitators, being installed in the lines as deemed advisable. Here again, one man will unload the quicklime and one man with a helper will be ample for the operation of other equipment—except for the actual unloading and stock-piling of the hydrated lime.

(*D*) *The Time Element.*

The influence of this factor is almost self-evident and needs very little discussion here. Referring back to the last assumed set of conditions, if the water treating plant uses lime continuously and the acid treating plant only occasionally, it would be doubtful economy to maintain a separate pump and pipe line to supply milk-of-lime to the latter point. A better plan would perhaps be to install a small crusher so it could discharge finely crushed quicklime directly into the waste acid stream, and to haul the lime to this crusher as it was needed. Or, if the stills consume lime twice as fast as the combined water and acid treatments, the lime-oil mixing and distributing system becomes relatively more important than the milk-of-lime equipment. Such considerations as these will be obvious as plans for the system are developed.

(*E*) *Quantity Used in Each Department.*

The actual quantity of lime consumed in any given length of time will, of course, determine the size and cost of separate equipment items required to serve each department. At times this may also dictate the combining of two units that would otherwise be separated. For example; a large stream of milk-of-lime serving the hydrogen sulphide absorption tanks might easily be tapped to furnish a small amount of lime to the water-treating plant; whereas, if both were small consumers, it would be better to have separate small lime feeders for each one. Or the fact that some one department uses large quantities of lime may call for the erection of extra storage tanks for quicklime, milk-of-lime or lime slurry.

(*F*) *Labor Costs Involved.*

The more we can mechanize our lime handling operations the greater will be the saving in manual labor required, and this may or may not be good economy, depending upon other conditions. Central mixing, hydrating or slaking plants; air conveyors; bucket elevators; crushers; pipe lines; reserve storage tanks, and many other mechanical units will eliminate hand labor and simplify operations. But they will be of value only in so far as they are utilized. Except for its "stand-by" value, the most efficient lime handling equipment becomes a liability if its interest and depreciation cost is greater than the cost of the manual labor it displaces. Wherever possible, the equipment should be planned on a unit basis, with space left for later installation of additional units, if they are found necessary.

(*G*) *Safety and Comfort of Men.*

Hydrated lime, delivered to the customer in heavy kraft paper sacks, is easily handled and offers very little in the way of discomfort or danger to the men handling it. They should wear gloves, of the gauntlet type, and also dust-tight goggles and respirators as a precaution against flying lime dust in case a sack becomes torn or broken while being handled. Any lime that accumulates on the skin can be readily dissolved by bathing with either a solution of sugar in water or with diluted vinegar. Another

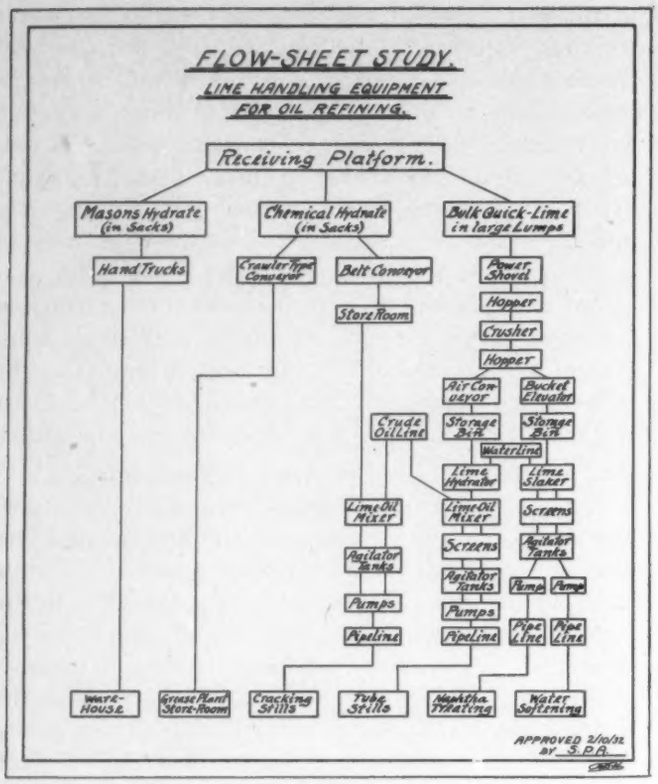


FIGURE 7

good application, which also tends to soften and soothe the skin, consists of a mixture of equal parts of olive oil and raw linseed oil. Hydrated lime exerts a drying action by absorbing water and natural oils from the skin, making it harsh and stiff, and may also be quite troublesome if it gets into an open cut or sore. It should by all means be kept out of the eyes, nose and throat.

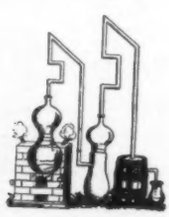
While quicklime is much more severe in its effects, it may be handled satisfactorily if a few simple precautions are observed. Quicklime dust, settling on the skin, absorbs the moisture in the skin just as eagerly as it does the water in a mortar box. Thus a burning, caustic action takes place which may cause troublesome burns or sores if neglected. The best remedy always being a preventative, the simplest way to avoid lime burns is to prevent the lime from reaching the skin. All men handling any dusty quicklime should wear dust-tight, loose fitting clothing, with dust-tight hoods covering the entire head and falling down over the shoulders. Gauntlet gloves, loosely strapped around and over the sleeves, and loose cloth leggins to keep dust from getting into the shoes or around the ankles, will complete a costume that affords almost perfect protection. It may be uncomfortable in hot weather and require the men to work in relays, but this is preferable to lime burns, doctor bills and lost time. If quicklime does get on the skin, it should be removed at once, by one of the above-mentioned simple methods.

Since it is easier to prescribe a remedy than to make the patient use it, we must give due consideration to the human element involved in the manual handling of lime. If only an occasional car of quicklime is handled, the working crew can probably be kept up to the mark on safety observance, but if the job is continuous there is likely to be a loss of efficiency due to failure to observe precautions, as well as considerable discomfort, dissatisfaction and lost time to the men. Therefore, the statement made above might well be amended to read "the surest way to prevent lime burns is to keep men away from the lime."

Consequently, the consideration of the human element will tend to offset the arguments given above in favor of hand labor, and should be given a great deal of thought in planning a properly functioning system of lime handling, to the end that it may be economical, efficient and safe.

SUMMARY

To illustrate the principles discussed in the preceeding paragraphs, we show in flow-sheet form a typical lime-handling installation, with indicated items of equipment (See Figure 7). Suitable variations, to fit any given set of local conditions, will readily suggest themselves, in the light of what has been said above.



Fundamentals of Condenser *Heat Exchange and Reboiler* *Design for* Natural Gasoline Rectifiers

I. N. BEALL

IN the accompanying article I. N. Beall discusses heat transfer problems as they apply specifically to high pressure rectification.

The conductivity of metal is not the greatest factor in determining overall coefficient of heat transfer. Metals, however, that resist corrosion are of real advantage, both from the standpoint of deterioration and reduction of deposits of scale and rust, which reduce the efficiency of heat transmission.

Because of the fact that heating is indirect, heat must pass through resistance in the form of metal, and through the practically stationary liquid or gas films adhering to both sides of the walls, and into the body of the liquid or vapor. The sum of all of these resistances determines the overall coefficient of heat transfer. Equations and detail discussion of their application to heat transfer problems in high pressure rectifying columns are presented.

KNOWLEDGE of the mechanics of heat transmission is of primary importance to the designing and operation of rectifying equipment. In the rectification of natural gas condensates the heat is usually supplied by means of condensing saturated steam. The major portion of the heat thus supplied is due to the heat evolved on condensation (latent heat). A much smaller amount of heat comes from cooling the water formed to the temperature at which it is discharged from the exchanger. The heat evolved must then be transferred to the medium which is heated to its boiling temperature and then partially or totally vaporized.

Because of the fact that the heating is indirect, the heat must pass through resistance in the form of metal and through the practically stationary liquid or gas films adhering to both sides of the walls and into the body of the liquid or vapor which is the receiver.

The sum of all these resistances determines the overall coefficient of heat transfer, which for convenience to engineering calculation is expressed as B.t.u. per square foot per hour, per mean degree temperature difference between its heating medium and the material heated. It is thus apparent that the amount of surface required for a given heat transfer operation is inversely proportional to the overall coefficient of heat transfer. Then only one-tenth of the surface area in the form of tubes or what not would be necessary for a condition where 1000 B.t.u. per, per square foot per degree F. temperature could be accomplished as would be required where only 100 B.t.u. /hr./sq. ft. /°F. could be transferred. One of the main objectives of all engineering design having to do with heating is to effect a high coefficient of heat transmission, thus reducing the construction and operation costs and at the same time producing more compact units.

DEFINITIONS AND SYMBOLS

The National Research Council Committee on Heat Transmission and the American Standards Association approve and recommend that the following definitions and symbols be adopted:

A—Area
t—Temperature °F. or °C
T—Temp. °Abs. = (460 + °F.) or (273 + °C)
L—Length of Path of Heat Flow
Q—Total quantity of heat transferred
T—Time in seconds, minutes or hours
q—Thermal transmission = $A(t_1 - t_2)$
k—Thermal conductivity (heat transferred per unit area and per degree per unit length)
1/k—Thermal resistivity
R—Thermal resistance (degrees per unit of heat transferred per unit of time)
C—Thermal conductance (heat transferred per unit time per degree)
C_a—Thermal conductance per unit area (heat transferred per unit time per unit area per degree)
h—Surface coefficient of heat transfer. . . . film coefficient of heat transfer (heat transferred per unit time per unit area, per degree)
U—Overall coefficient of heat transfer thermal transmittance per unit area (heat transferred per unit time per unit area per degree over all)

Most engineering calculations pertaining to heat transfer are made using the English engineering units, and coefficients, i.e.

The unit of area	A	= 1 square foot
Temperature	t	= Degrees Fahrenheit
Temperature	T	= Degrees Fahrenheit Abs.
Unit of thickness		= 1 inch
Unit of heat quantity		= 1 B.t.u.
Unit of time		= Second, minutes, hrs.

The coefficients of heat transfer are expressed as

B.t.u. per hour per square foot per degree Fahrenheit temperature difference. Once the coefficient of heat transfer has been determined, the heat flow may be calculated from the equation $q = A\ (t_1 - t_2)$. This coefficient is in most cases the element of guesswork.

HEAT TRANSMISSION AS APPLIED TO NATURAL GASOLINE FRACTIONATION

In natural gasoline rectification heat is continuously supplied and continuously abstracted from the system. The primary source of heat supply is in the form of steam. Heat exchangers help to conserve this heat and increase its effectiveness. Water offers the principal means for heat abstraction although here again heat exchange or artificial refrigeration may, and is as a rule, resorted to. Heat is transferred through metal walls in the form of tubes and may be between (1) liquid and liquid (2) condensing vapor and liquid, (3) condensing vapor and vaporizing liquid, (4) liquid and vaporizing liquid.

Heat transfer is essentially a surface phenomenon and depends upon a temperature difference between the heating medium and the materials to be heated. The coefficient of overall heat transfer is subject to great variations, ofttimes of which the least contributing factor is the metal of the tubes. Thus, for example, the coefficient of heat transfer for condensing steam may be as high as 2000 B.t.u. per square foot per hour per degree Fahrenheit temperature difference, while a heated fixed gas over the tubes may be as low as 8 B.t.u. per square foot. It is evident that the surface requirements as calculated for steam would be painfully inadequate if one applied the same to a superheated gas.

The basic concept of heat transfer is that the number of molecules which impinge the surface and yield up their quota of heat determine the amount of heat that will pass from the warmer to the colder medium. If a large number of molecules with a high heat content per mol impinge the surface as in the case of steam, the coefficient of heat transfer is large. Metals differ considerably in their resistance to heat flow, but the bugaboo of the design engineer is not so much the metals used as it is the films which form on the surfaces of the metals. These films are practically stationary when compared to the medium passing over the surfaces and set up high resistance to heat flow.

A little air in steam may reduce the transfer per square foot from 2000 to 200 or even less, for the reason that the air or oxygen is more strongly attracted to the surface and forms films of high resistance. Likewise, the cooling surface in condensers would be a variable requirement not based directly on the number of B.t.u. to be abstracted over a unit of time but upon other major factors, such as the amount of uncondensable gases. To be specific, it would require more surface to abstract one million B.t.u. from gas partially condensing than it would require for a vapor yielding the same quantity of heat and totally condensing. Heating surface is expensive and an excess over requirements is an insurance ofttimes too costly to be warranted.

The overall coefficient of heat transfer U for parallel flow is

$$U = h_1 + h_2 + h_3, \text{ etc. and for series flow is}$$

$$\frac{1}{U} = \frac{1}{h_1} + \frac{1}{h_2} + \frac{1}{h_3}, \text{ etc.}$$

Thus, for example, taking the surface coefficient of heat transfer for evaporating natural gasoline in a column kettle as $150 = h_1$ and for condensing steam $h_2 = 2000$, then

$$\frac{1}{U} = \frac{1}{150} + \frac{1}{2000} = \frac{43}{6000} \text{ whence } U = 140.$$

It can be shown that the coefficient of heat conductivity for a metal is a small factor in the overall coefficient U. Thus, for example, at $h_3 = 1020$ per inch thickness in tubes ¼-inch thick, $h_3 = 4080$, or still at $h_4 = 300$, and in ¼-inch $= 1200$.

$$\frac{1}{U_1} = \frac{1}{150} + \frac{1}{2000} + \frac{1}{4080}$$

$U = 135$ B.t.u. for aluminum

$$\text{and } \frac{1}{U_2} = \frac{1}{150} + \frac{1}{2000} + \frac{1}{1200}$$

$U_2 = 125$ B.t.u. for steel

$$\text{or } \frac{U \times 100}{U_2} - 100 = 8\% \text{ greater for aluminum}$$

The figures used are reasonable approximations of real values and illustrate what a small factor the metal is in the overall coefficient of heat transfer. It is a rather common error even among engineers to assume that the heat transfer per square foot per hour per degree temperature difference is proportional to the conductivity of the metal used as a construction material. On this basis the overall heat transfer for aluminum over steel would be

$$\frac{4080 \times 100}{1200} - 100 = 240\% \text{ greater}$$

whereas an 8% increase would be more nearly correct. If any great increases in overall heat transfer are to be attained it will have to come from other means than through variation in the metals used for heating walls. The surface conditions of the wall is of far greater importance insofar as such applies to heat transfer efficiency.

SURFACE FOR COLUMN REBOILERS

Steam is as a rule used as the heating medium through the tubes. These tubes are immersed in natural gasoline which is vaporizing. The amount of heat required for vaporization has been estimated by methods described in previous articles, say, for example, as 200,000 B.t.u. per hour. How much tube surface in square feet will be required? The overall coefficient of heat transfer U_2 for steel tubes under these conditions (see preceding calculations) has

been estimated as 125 B.t.u. per square foot per hour per mean degree temperature difference. Let us say the steam temperature is 220°F. and the kettle temperature 190°F. Then:

$$\frac{200{,}000}{125\ (220-190)} = 53\text{-}1/3 \text{ square feet of surface required}$$

If one inch standard tubes were used the mean of the external and internal surface would require approximately 3.28 lineal feet per square foot or 53-1/3 x 3.28 = 175 feet or in round numbers 30 lengths of six feet each if such length met the space requirements. For steam containing air the heat transfer coefficient might drop to as low as 25, in which case 875 lineal feet of pipe would be required. Oil in the steam or dirty pipes could still further cut down the heat transfer coefficient. The designing engineer, however, usually figures that the worst possible operating conditions will exist and makes due allowance by incorporating ample heat transfer surface. The purchaser, however, pays the bill which after all is perhaps as it should be as the fault lies in that direction. It is easier to put in tubes than make excuses for performance.

CONDENSERS

More surface is required to abstract the same number of B.t.u. for partial condensation than is required for total condensation. The reason for this is that the coefficient of heat transfer is lower for a gas than for a condensing vapor. Partial condensers for natural gasoline rectifiers should allow for not more than 25 B.t.u. per square foot per degree per hour. Assuming maximum operating flexibility as the objective, the tube surface of the reflux condenser would be approximately five times that of the reboiler tubes for equal temperature difference in both kettle and condenser.

The heat from the vapors and gases passing through the condenser, must pass through compound resistance, that is, the heat passes to the tube wall through a film on the surface, through the metal wall, and then through the film on the surface of the metal on the opposite side, and into the cooling medium. Let us take an example by way of illustration. In order to determine the coefficient U, A is taken = 1 and $t - t_2 = 1$. The equation then is—

$$U = Q = A\ (t - t_2), \frac{1}{\frac{L_1}{h_1} + \frac{L_2}{h_2} + \frac{L_3}{h_3}}$$

Take $L_1 = .01$ inch $= \frac{.01}{12} = .00083$ ft.

$L_2 = .01$ inch $= \frac{.01}{12} = .00083$ ft.

$L_3 = 0.24$ inch $= \frac{0.24}{12} = .02$ ft.

Where L_1 and L_2 are film thicknesses and L_3 is the thickness of the tube wall h_1, h_2 h_3 = thermal conductivity of fluid films and metal in respective order.

$h_1 = .07$ for vapor film
$h_2 = .35$ for water film
$h_3 = 40$ for metal wall

Substituting numerical values in the equation,

$$U = 1 \times 1 \left(\frac{1}{\frac{.00083}{.07} + \frac{.00083}{.35} + \frac{.02}{40}} \right) = 67 \text{ B.t.u.}$$

For clean tubes and optimum conditions the heat transfer as calculated would amount to 67 B.t.u. per square foot per hour per degree F. temperature difference between the water and the vapors. The above equation is useful for purposes of study as it will be found that small changes in the values of h_1 cause relatively great changes in the value of U. The point of attack then to gain increased heat transfer efficiency would be on the vapor side, next on the cooling liquid side and last upon the metal wall itself. It is of small gain to increase the conductivity of the resistance which is already high.

In the case of cooling methane, a film coefficient of 0.02 would probably give more nearly accurate results than the vapor film $h_1 = .07$ used in the example. This would make U = 22 B.t.u. An evaporating liquid on the cooling surface side would increase the value of U by increasing the conductivity in that film within the range of 150 to 1000. Liquid hydrocarbon through the tubes for cooling would lower the value of U and increase the cooling surface requirements.

Suppose an evaporating liquid is used for the cooling medium having a value $h_2 = 150$. Substituting this value for h_2 in the equation first given U = 70 B.t.u. as compared to 67 B.t.u. If, however, h_1 can be increased from .07 to .2 then U = 141. It is apparent from the illustration given that any marked advance in the overall coefficient of heat transfer must come from the side of the condensing gasoline vapors. This can, to a degree, be accomplished by an increase of velocity in these vapors over or through the condenser tubes. An increase of pressure also favors a reduction in tube surface as the increased concentration of the vapors causes more molecular contact of the surface which yields up greater heat per unit of area. Working against this increase in density is a simultaneous increase in viscosity. The decreased volume necessitates a decrease in the cross section vapor area in order that this velocity may remain undiminished.

NUSSELT'S THEORY OF THE MECHANISM OF CONDENSATION

Nusselt (Zeit V. d. I. **60,** 541 (1916) gives a mathematical treatise on the theory of vapor condensation. This mathematical discussion includes the five following generalized cases:

1. Vapor condensing on an inclined tube or wall.
2. Vapor condensing on a horizontal tube.
3. Saturated vapor passing over a surface on which condensation takes place.
4. The condensation of superheated vapor on surfaces.
5. Impure vapors condensing on any surface.

All five cases are of application to the design of rectifying systems for natural gasoline condensates.

Under case Number 1, the integrated equation for vertical tubes is

$$U = \frac{0.943 \sqrt[4]{A}}{\sqrt[4]{H\,(t_v - t_w)}}$$

where H = height of tube in feet
tv = vapor temperature °F.
tw = wall temperature °F.

$$A = \frac{L\rho^2 k^3}{z}$$

For tubes sloped from the horizontal, the equation is:

$$U = 0.943 \sqrt[4]{\frac{L\rho^2 k^3 \sin \phi}{z\,H\,(t_v - t_w)}}$$

L = latent heat in B.t.u.
ρ = specific gravity (density)
ϕ = angle from horizontal
z = viscosity $\frac{\text{lb./sec.}}{\text{ft.}^2}$

The above equations would apply to steam condensing on vertical tubes or tubes at an angle from the horizontal. The same applies to the condensation of any pure hydrocarbon vapor under similar conditions.

Case 2.—For average conditions:

$$U = \frac{0.725 \sqrt[4]{A}}{\sqrt[4]{D\,(t_v - t_w)}}$$

where D = diameter of tube in feet.

This case is directly applicable to cases where cooling liquids such as water or oil is passed through the tubes and vapors pass over the outer surfaces. Reflux condensers of the overhead type may fall within this category as also may total condensers.

Case 3.—According to Nusselt:

$$U_{mv} \sqrt[4]{\frac{H}{a}} \text{ is a function of } \frac{b}{\sqrt[4]{\frac{H}{a}}}$$

$$a = \frac{L\rho^2}{4k\,z\,(t_v - t_w)}$$

$$b = \frac{C_3\, w^2\, \rho\, v}{3\rho}$$

So far as is known to me, this case has been applied only with steam.

Case 4.—The equations are too complicated for practical use. The quantity of heat as superheat is usually small as compared to the latent heat, so little error is introduced by assuming the vapor to be saturated.

Case 5.—While it is known that non-condensable gases exert a marked influence on the heat transfer coefficient, there are, at present, no equations of general application. It is assumed that in such condensations, there are two films, that is, a layer of condensate on the cooling surface of the metal and the other a gas film on the surface and a part of the condensate film. Colburn and Hougen, (J. I. E. C. May, 1930, pp. 527) have given equations for calculating the thickness of these liquid condensate films for vertical and horizontal pipes. These equations are given as follows:

Vertical pipe:

$$\phi = \sqrt[3]{\frac{3\,C\,\mu}{\rho^2\,g}}$$

Horizontal pipe:

$$\phi = \sqrt[3]{\frac{1.5\,\mu\,d\,a}{\rho^2\,g}}$$

where d = diameter of pipe
ϕ = thickness of layer
C = rate of flow of condensate down vertical pipe per unit length of circumference
a = rate of condensation per unit area of horizontal pipe
μ = viscosity of condensate
ρ = density of condensate
g = acceleration of gravity

The heat transmission coefficients for the films are:

For vertical pipe:

$$h = k \sqrt[3]{\frac{\rho^2\,g}{3\,C\,\mu}}$$

For horizontal pipe:

$$h = 0.78 \sqrt[3]{\frac{\rho^2\,g}{1.5\,d\,a\,\mu}}$$

k = thermal conductivity.

It is evident that all terms of these equations must be expressed in "consistent" units. That is, if results are to be in B.t.u./sq. ft./°F/hr., the diameter of the pipe, thickness of film, etc., must be in feet, fluid density ρ = lbs. per cu. ft., viscosity, μ = lbs. per second per foot x 3600. To convert from c.g.s. or absolute units, "Poises," that is from gms./sec./cm. to English units lbs./sec./ft. multiply by 0.0672.

LOGARITHMIC MEAN TEMPERATURE DIFFERENCE

The logarithmic mean temperature difference is used to a much greater extent in heat transfer calculations than the arithmetic. The cooling medium flows on one side of a surface as over tubes and the liquid gas or vapor flows on the other side. There is a gradual increase in the temperature of the cooling medium and a gradual decrease in the tempera-

ture of materials undergoing cooling. Assuming uniform temperature variations in both the equations is:

$$\Delta\ t_{av} = \frac{\Delta t_1 - \Delta t_2}{\ln\left(\frac{\Delta t_1}{\Delta t_2}\right)}$$

For example, water at 80°F enters a counter current condenser and leaves at 120°F. and the vapor enters at 135°F. and leaves at 90°F.

$$\Delta t_{av} = (135 - 120) - (90 - 80) = \frac{5}{0.4055} = 12.3°\text{F.}$$

In a case where the overall coefficient heat transfer, U = 125, the heat transferred per hour per square foot would be

$$12.3\ U = 12.3 \times 125 = 1537.5 \text{ B.t.u.}$$

Suppose then the total amount of heat to be removed in condensing had been calculated as 250,000 B.t.u. per hour. Under the above conditions the amount of surface required would be

$$250{,}000 \div 1537.5 = 162.5 \text{ sq. ft.}$$

EFFECT OF WATER VELOCITY ON COOLING

An approximation of the effect of water velocity on the cooling may be had by the equation:

$$h_w = 450\ V^{-\frac{3}{4}}$$

where V = water velocity in ft. per second.
At 5 ft. per second,

$$h = 450\ (5)^{\frac{3}{4}} = 450 \times 3.34 = 1460$$

whereas at 1.0 ft./sec.

$$h = 450$$

and at 10 ft./sec.

$$h = 450 \times 5.623 = 2535$$

In this article the writer's intention has been to acquaint the reader with certain fundamental principles which affect natural gasoline fractionator design. The writer has observed cases where hot oil was circulated through reboilers intended for use with steam, oil substituted for water through condensers and other equally bad examples of ignorance of the principles of heat transfer. In the purchase of rectifying equipment, a knowledge of the principles involved would be of invaluable assistance in the selection.

As stated previously in this article, the conductivity of metal is not the greatest factor in determining the overall coefficient of heat transfer. However, materials which resist corrosion are of great advantage, not only from the standpoint of deterioration but also from the fact that scale and rust enormously reduce the efficiency of heat transmission.

For reboilers using saturated steam, short pipes of small diameter are to be preferred, using where possible a high steam pressure. It matters little whether or not the tubes are thick walled or thin walled as more attention should be given the polish and smoothness of the surface and then their construction and arrangement. Totally immersed tubes give good results, but the probable highest heat transfer is attained where the liquid is forced over the tubes at high velocity. An increase in velocity reduces the thickness of the film thus permitting faster heat transfer. In the partial and total condensers where water is the cooling medium through the tubes, and vapors condense on the surface, care should be exercised to see that the proper vapor velocities are insured at the pressure where their volume is greatly reduced. The water, or other liquid for that matter, should pass through the tubes in turbulent flow so as to give the maximum surface effectiveness. But perhaps above everything else is the fact that a high overall coefficient of heat transfer per square foot increases the sensitivity of temperature control because of the lower resistance offered which reduces the temperature lag.

PART 3

Gases Produced... *from* Cracking Oil in Vapor Phase

M. B. MARKOVICH and B. B. PIGULEVSKI
Engineer Technologist, Liningrad, Russia

THROUGH a cooperative arrangement with the Petroleum Division of the American Chemical Society a series of technical articles will be presented in THE REFINER AND NATURAL GASOLINE MANUFACTURER *for distribution in English in this country and abroad. The articles are translated from the Russian by members of the Petroleum Division of the American Chemical Society, thus making available the results of research carried out in the scientific laboratories of the Soviet.*

The accompanying discussion, constituting Part 3 of the first of the series, deals with gases produced by cracking oil in the vapor phase. This gaseous production of vapor phase cracking is one of the richest and most accessible sources of raw material for the synthesis of a very large number of chemical products. The presentation of this work will be concluded in an early issue.

6. DISTRIBUTION BY COMPOSITION OF GASEOUS PRODUCTS OF VARIOUS SOURCES

We made studies of the products obtained only at "Napthagas" Refinery under normal refinery conditions. The average operating temperature of the process was between 580°-620° C for two and a half years. During the same period of time we were doing our research work. The hourly throughput of the retort was between 13 to 20 Kg. and in only a few cases up to 40 kg. (trial runs of gasoline). The throughput was about 15 kg. per hour in average. The main raw material was the light crude oil from Baku (usually Soorahan crude); in individual cases the raw material was of another origin,—mostly the motor fuel from Koustantin Refinery of Embanaphtha.

The figures for (fat) wet gases (that is, products of the rectification of gases) were almost constant—from 20 to 24% based on the refined naphtha, and only in a few cases somewhat below 20% due to some particular reasons. The obtained amount of fixed gases varies to a greater extent.

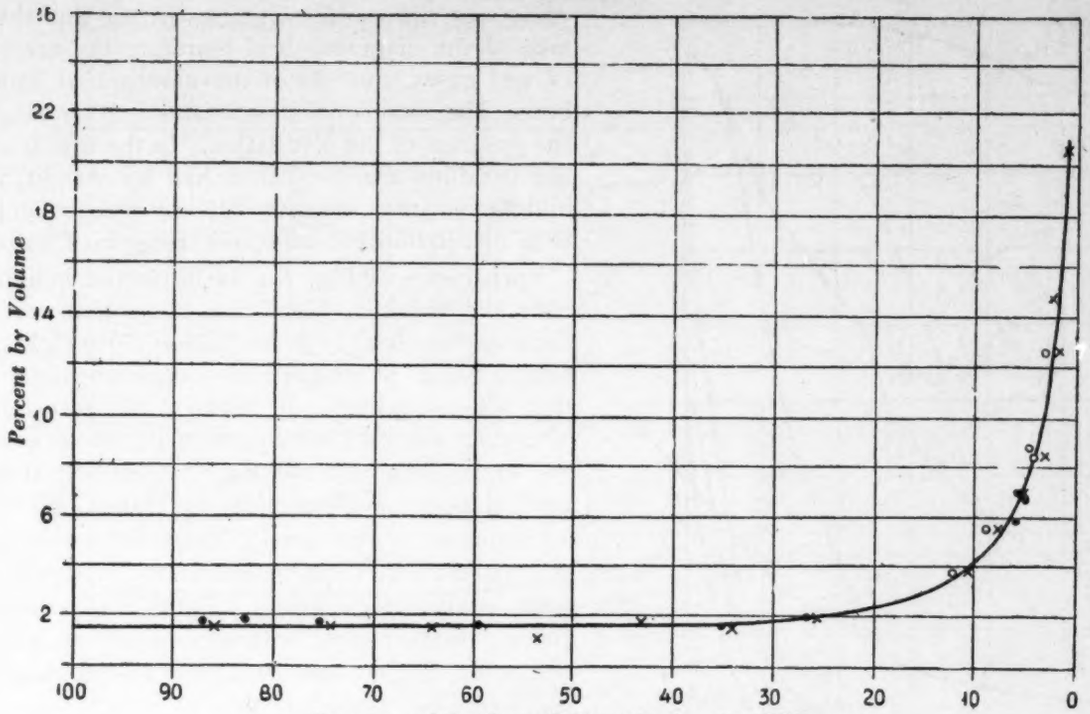
Besides the gross fraction of wet gases we were investigating also the products of their secondary distillation performed under regular refinery conditions. We were producing the last at the refinery since 1926 under the name of "ethylene concentrate" and "propylene concentrate". They are the fractions of a rough fractional isothermae vaporization. These fractions correspond to the maximum of the curves of isothermal distillation (Figs. 8 and 9) accumulated in great quantities in one vessel.

Figures Nos. 8 and 9 are diagrams of analysis of products obtained from isothermal vaporization of three gases of entirely different origin.

It is very clearly seen, that the content of gaseous fractions of isothermal vaporization does not depend on the kind of gas we deal with; but only on the pressure (at a constant temperature) at which the given fraction was obtained (within reasonable limits of accuracy). In other words, at a given pressure of the vessel the composition of the obtained gases does not depend on the origin within reason, but is only a function of pressure. This is in accordance with our understanding of physical chemistry of the processes obtaining final product and of the distillation.

If we will use the data from Figs. No. 8 and 9 in making a diagram showing weight of the distilled gas on the abscissa instead of pressure, such a co-incidence of curves may not occur. The difference in curves for normal blaugas and propylene concentrate, very clearly seen from comparison of Figs. No. 4 and 5, is caused by a greater content of propylene in the last. We have to conclude that we cannot get good fractionation by the method of fractional distillation used to make the propylene concentrate, because the total content of C_3H_6 in the last is 22 to

FIGURE NO. 9



25% more than in a unit volume of normal blaugas (it is true that the comparative content of heavier components is considerably smaller if the last portion of the curves of Figs. Nos. 4 and 5 are compared). Therefore, the separation of concentrated olefins should be obtained not by the fractional concentration but by the secondary rectification of wet gases.[33]

The conclusions of this chapter are as follows:

(1) The relative content of the individual olefins in the refinery products is stable (at the operating temperatures of refinery cracking processes).

(2) The amounts of separate olefins in the fractions of isothermal distillation differ within the error of the analysis for each given pressure and for products of various origins. The curves "percent by volume"—pressure (see Nos. Figs. 8 and 9) are equivalent to each other for most of the different products subjected to investigation.

(3) The curves of the content of separate olefins are different for various products, depending on the volume and weight of distilled material and are typical in respect to the actual content.

(4) The method of the multiple isothermal va-

TABLE NO. 7

SUMMARY OF VOLUMETRIC DATA ON CONTENT OF INDIVIDUAL COMPONENTS IN GASEOUS FRACTIONS OF ISOTHERMAL VAPORIZATION OF WET GASES

(According to Figure No. 1)

Gaseous Fractions by volume in m³	Volumes in Percent							
	iC_4H_8 and Higher	C_4H_6	nC_4H_8	C_3H_8	C_2H_4	Σ Unsaturates	Saturates in saturated Gases*	H_2 %
0 -0.5	from 1.4% to 1.8% (1.6% in average)	Average .8%	from 1.4% to 1.8% (1.6% in average)	6.0	16.0	26.0	61.0	13.0
0.5-1.0				6.0	16.5	26.5	63.5	10.0
1.0-1.5				6.5	18.5	29.0	63.0	8.0
1.5-2.0				7.5	21.0	32.5	61.5	6.0
2.0-2.5				8.5	24.0	36.5	59.5	4.0
2.5-3.0	1.8	1.0	1.7	9.5	27.5	41.5	55.5	3.0
3.0-3.5	2.0	1.3	2.0	11.0	32.5	48.5	50.0	1.5
3.5-4.0	2.3	1.7	2.3	16.5	38.0	60.5	39.0	0.5
4.0-4.5	3.4	2.0	3.1	26.0	33.0	67.5	32.5	...
4.5-5.0	5.2	3.0	4.3	38.5	23.0	74.0	26.0	...
5.2-5.5	10.0	6.5	8.5	54.0	6.0	85.0	15.0	...
5.5-6	28.0	12.5	17.5	49	...	97.0	3.0	...
Totals In Round Numbers	5.1%	2.7%	3.9%	19.0%	21.3	52.0%	44.2%	3.8%

*Saturated gases include CO, CO_2, O_2 and N_2.

FIGURE NO. 10

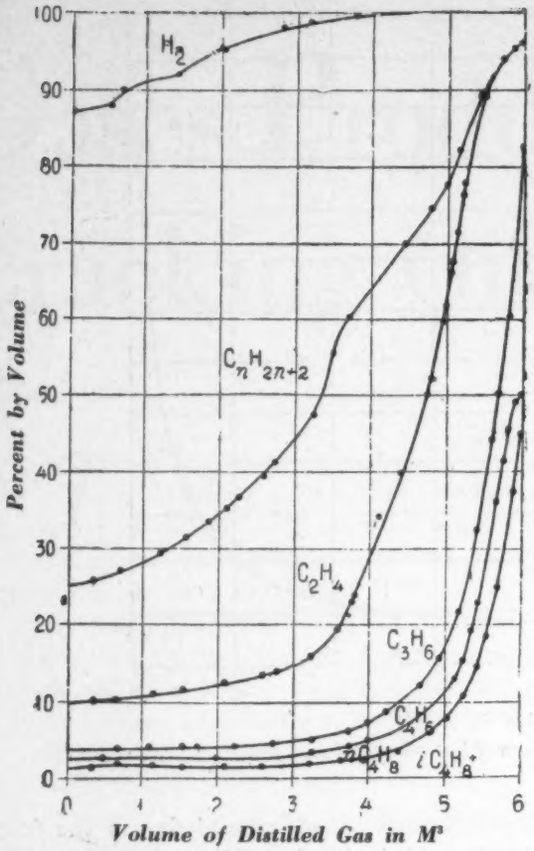


Diagram of Composition of Gaseous Fractions of Isothermally Vaporized Wet Gases in Percent by Volume

porization does not give good fractionation. To get this, it is necessary to use a rectifying column.

7. THE FINAL SUMMARY OF THE CONTENT OF THE WET GAS FRACTIONS

Table No. 7 and Fig. No. 10 are the final summaries of wet gas fractions according to composition (in volumetric relation). Fig. No. 10 is made so that the first curve—that of "isobutylenes and higher" is plotted the ordinary way laying out portions of the ordinate from the corresponding points on the abscissa. Next curve, — divinyl curve — is made by laying out volumetric data on the ordinate on top of the first curve. Thus the second curve represents the sum of isobutylene and divinyls in relation to the abscissa, and the area between the first and the second curves give the quantity of divinyl. The third curve, that for n-butylene, is made the same way as the second curve. With this method of plotting, the areas of the diagrams, limited by the curves, represent the total content of the components of the mixture, and the parts cut off by the curves from any vertical, indicate the composition of the distillate. The table No. 8 and Figure No. 11 are more comprehensive data. Here the data is expressed in weights. The principle of formation of Fig. No. 11 is similar to that used for Fig. No. 10.

By integration of this data we have an opportunity to judge about the total content of separate components. From these figures we see that the main area of the diagram,—and therefore the main mass of wet gases, consists of the unsaturated hydrocarbons. The number of unsaturates is increasing with the progress of the distillation. In the first fractions, the paraffins are more than half by weight, in the middle cuts they are only 23% by weight, and after 80% distillation the saturates disappeard entirely.

Each curve of Fig. No. 12 is plotted individually from the abscissa. Here they show that maximum for propylene is at 73% distillation (by weight). The boiling point of propane is somewhat higher than that of propylene (38 and 47°C. respectively). Therefore the cuts which are richer in propane are not to be found on the Fig. No. 11, left from the vertical corresponding 73% distillation. The area for saturates is very small. Therefore we can arrive at a conclusion, (also based on the analysis of the curve of average molecular weights of paraffines (see above)) that propane is in subordinate quantities in our gases. Butane and isobutane are practically absent (compare table No. 10).

By studying the Fig. No. 12, it can be easily noted that there is more propylene in the unsaturated portion of wet gases than any other compounds. It is

FIGURE NO. 11

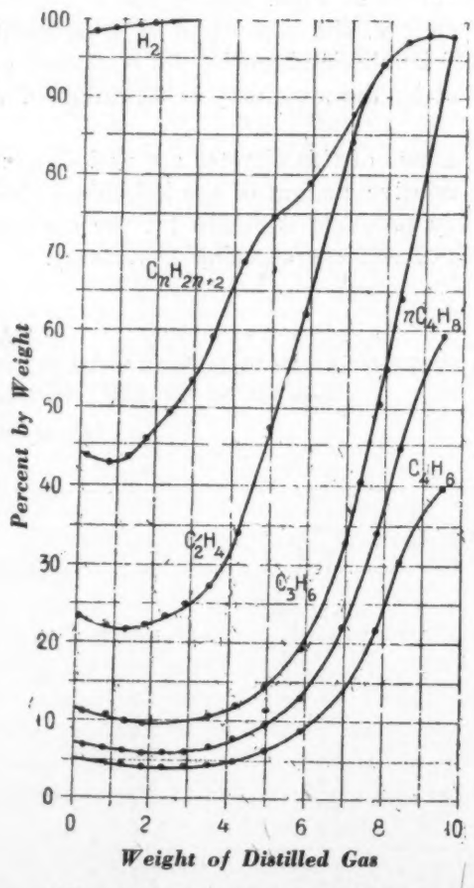
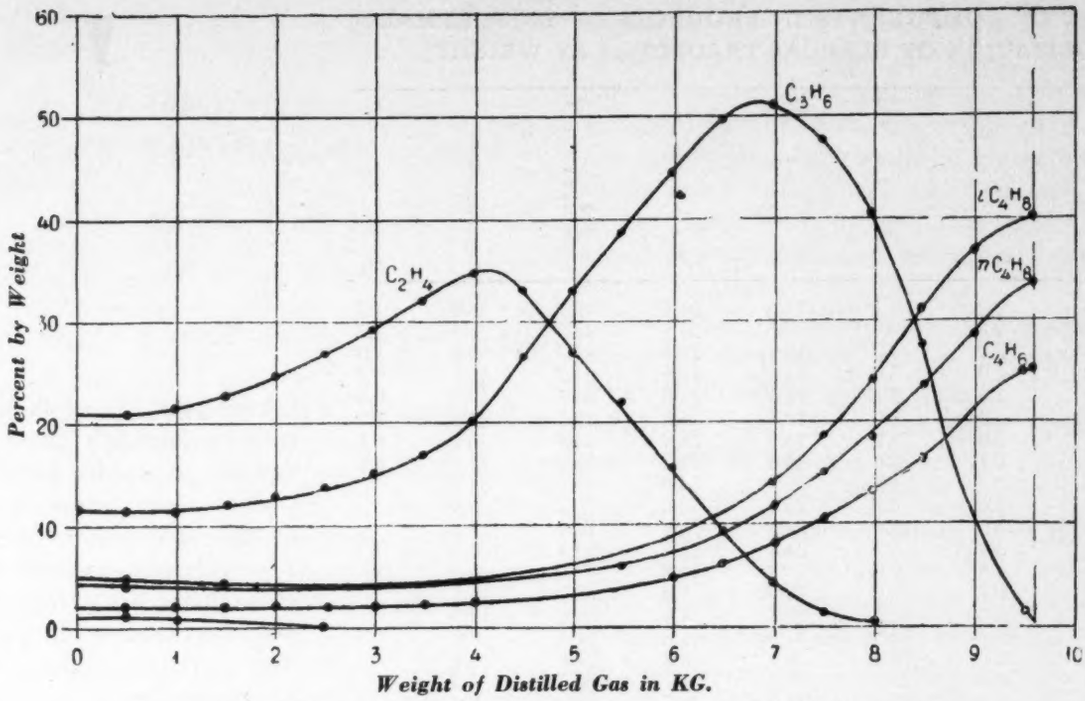


Diagram of Composition of Gaseous Fractions of Isothermally Distilled Wet Gas in Percent by Weight

FIGURE NO. 12



Content by Weight of Individual Olefins in the Products of Isothermally Vaporized Blaugase Fraction

almost one quarter by weight of the whole gas and 34.8% by weight of the unsaturates. A great content of C_3H_6 and the absence of near by boiling individuals (besides propane) permit us to obtain gaseous fractions containing 50% of C_3H_6 even with so imperfect a method of separation as the isothermal vaporization.

Ethylene is occupying the second place in respect to its quantity (17.1% of the weight of the whole gas and 24.5% of the weight of unsaturates). The maximum of ethylene is not as great as that for propylene. The curve of variation of its content (See Fig. No. 12) is very flat.

The reason for it is as follows: (a) The nearby boiling ethane is in great quantities in our gases;

(b) The ethylene fractions vaporize at high pressures at which the solubility of hydrogen and methane is very great; the last carry over a great quantity of ethylene with their stream during the vaporization, even at the highest pressures of distillation.

(c) Ethylene is a fixed gas only dissolved in wet gases under the conditions of distillation (critical temperature plus 12°C.)

The group of unsaturates with four carbons is represented by all possible gaseous representatives of mono and diolefins (that is by both normal butylenes, isobutylenes and divinyls).

The possibility of presence of allylene remains to be seen. The higher wet unsaturates with one (Methyl, ethylethylene, trimethylethyene, etc.) or with two double bonds (isoprene, piperylene, cyclopentadiene, etc.) are present in the heaviest gaseous fractions, but in very small quantities. In most cases, they are included in the sum of isobutylenes ("isobutylenes and higher"). What are the homologues of these series, and in what relative quantities they are, we cannot say as yet.

As it was indicated in the chapter about the method of analysis, we can find the sum of n-butylene plus divinyl only by indirect means (by the difference of sp. gravity). The last, as we noted, is determined by another method which gives a considerable error. Therefore the division line on Figs. 10 and 11 between the areas of divinyl and n-butylene and between the areas of n-butylene and propylene, especially the first, are determined with less exactness than the other curves. There may be variations up to 5%.

Figures for normal butylene are used for α and β isomers because we do not know yet the method of analysis permitting us to determine them separately or isolate them from each other. The totals of the Table No. 8 show that the quantity of isobutylene is greater than that of other hydrocarbons with 4 Carbon atoms (11.9% of this total weight of gas and 17.1% of the weight of unsaturates). However, it is necessary to make a correction here. As we just saw, we were discounting a certain part of heavier admixtures together with isobutylene. The average molecular weight of gas, absorbed in the first absorber (for the heavy fraction having a significance here) are de-

TABLE NO. 8—Summary 3rd.

CONTENT OF COMPONENTS IN PRODUCTS OF ISOTHERMAL VAPORIZATION OF BLAUGAS FRACTION (BY WEIGHT)

Points on Abscissa of Distillation: of Distilled kg.	i C_4H_8 / higher Hydrocarbons	C_4H_6	C_4H_8	C_3H_6	C_2H_4	Total of Unsaturates	Saturates, etc.	H_2
0	4.8	2.2	4.1	11.6	21.0	43.7	55.0	1.3
0.5	4.6	2.0	4.0	10.6	21.1	42.3	56.5	1.2
1.0	4.4	2.0	4.0	10.4	21.4	42.2	56.8	1.0
1.5	4.0	2.0	3.9	11.7	22.6	44.2	55.1	0.7
2.0	3.9	2.0	3.9	12.4	24.5	46.7	59.9	0.4
2.5	4.0	2.0	3.9	13.5	26.8	50.2	49.6	0.2
3.0	4.1	2.0	3.9	14.9	28.9	53.8	46.1	0.1
3.5	4.3	2.1	4.6	16.6	31.8	58.9	41.0	0.1
4.0	4.6	2.3	4.4	19.9	34.4	65.6	34.0	
4.5	5.1	2.6	4.7	25.0	32.8	70.2	29.8	
5.0	5.8	3.0	5.2	31.5	26.9	72.4	27.6	
5.5	7.0	3.6	5.7	34.8	21.1	75.8	24.2	
6.0	8.5	4.5	7.0	44.2	14.8	70.0	21.0	
6.5	10.7	6.2	9.0	49.0	9.0	83.9	16.1	
7.0	13.9	8.0	11.5	50.6	4.0	88.0	12.0	
7.5	18.5	10.4	14.6	47.0	1.2	91.7	8.3	
8.0	24.0	13.0	18.4	39.0	0.2	94.6	5.4	
8.5	30.5	16.0	23.2	27.0	..	96.7	3.3	
9.0	36.2	22.0	28.1	11.7	..	98.0	9.0	
9.5	39.2	24.0	33.6	1.0	..	97.7	2.2	
%	11.90	6.60	9.86	24.30	17.13	69.79	29.96	0.25
Weight in Round Figures	11.9	6.6	9.0	24.3	17.1	69.8	30.0	0.2

termined as 62.5, at the same time the theoretical figure for molecular weight of isobutylene is 56.

Taking into consideration this data we can figure that $\frac{11.9 \times 56}{62.5} = 10.3\%$ of the weight of gas is isobutylene proper (or 14.8% of the weight of the unsaturates); the balance 1.6% consists of admixture of vapors of hydrocarbons with five or more atoms of carbon.

A certain amount of amylenes (see above division 2-4) is discounted by the same method in normal butylenes (9.9% and 14.2% respectively). Calculations by the molecular weight, analogous to one just mentioned, cannot be employed here, because the very figure for n-butylene was obtained by the same method. On the other hand, by using up the material resulting from our research, we can assume that there are about .9% (of this total weight of gas) of vapors of amylenes, etc., in the figures for n-butylene.

All the butylenes are in greater quantities than ethylene in wet gas fractions (21.8% and with corrections 19.3% against 17.1% of ethylene). There are more unsaturated hydrocarbons with four carbon atoms (butylenes and divinyls) than propylene (25.9 and 24.3%).

The maximum points of the curves for all hydrocarbons with four carbon atoms are noticed at the end of distillation, since the boiling points (which are between 6°C and 4°C and only for pseudo butylenes plus 1°) of these hydrocarbons approach those of the liquids. A sudden break in the curves at the points of maxima makes one suspect the presence of a considerable amount of these gases in the next fraction of the plant rectification, that is in the light cracked gasoline. This was discovered by us in time. (See below).[34]

The curves of Figs. 10, 11 and 12 can be used as equilibrium curves for designing of fractionating equipment for gas obtained from vapor phase cracking.

The data of Tables Nos. 7 and 8 with certain corrections permits us to make the following table of composition of wet gas fraction (by weights):

TABLE 9

Hydrogen	.2%
Saturated Hydrocarbon of average mol. weight of 21	29.6%
Inert gases (CO, CO_2, N_2, etc.)	.4%
Unsaturated hydrocarbons	69.8%
	100.0%

Unsaturated hydrocarbons consist of the following components:

		By weight*	Relative	in the unsaturated
Ethylene		17.1		24.5
Propylene		24.3		34.8
n-Butylene	9.0		12.8	
Divinyl	6.6		9.5	
i-butylene	10.3		14.8	
Vapors of unsaturated hydrocarbons with five or more carbon atoms	2.5		3.6	
		28.4		40.7
Total		69.8		100.0%

There is nothing in the literature regarding the composition of unsaturated hydrocarbons in the gases of cracked naphtha. The most complete data

for gases similar to ours, namely for gases of primary carbonization of coal, are obtained by Manning and his assistants.[35]

TABLE NO. 10

We will give a comparison between ours and Manning's results:

	C_2H_4	C_3H_6	C_4H_8	C_4H_6
Our figures in volume (Table No. 7) in respect to unsaturates for 560—580C.	41.0%	36.5%	17.3%	5.2 %
Manning's figures for 600° C.	48.6%	25.0%	26.4%	.06%

Taking into consideration the difference in methods of analysis (compare all said about it in the first part of this paper), the difference in temperatures of pyrolysis, etc., we have to admit that the general relation between the olefins is the same in both cases.

The only serious deviation is in the content of divinyls which probably was caused by the difference in heating (it is possible that the cracked gases were a longer time in the zone of high temperature in Manning's case).

8. THE COMPOSITION OF SATURATED FRACTIONS

This cut is the lightest fraction of the cracked gas rectification; its components are fixed gases. It is necessary to rectify them because of high solubility (especially at such a high temperature) in the main mass of wet gases. For this reason and also because of imperfectness of our columns, it is imposible to get a good separation, and, therefore, there are heavier hydrocarbons up to butylene in the fixed gas fraction.

Variation in quantities and in composition of fixed gases is noticed to a greater extent than in case of wet gas fractions. Here the change of the raw material and the temperature make a greater effect than in the other case. These variations are caused also by the intermittent process of rectification of gases (fixed gases are released sporadically without direct control of their composition).

In average the amount of fixed gases in relation to that of the total gas may be accepted as 20% by weight and seldom higher than that.

Weight of one m^3 of fixed gas at O°C and at 760 mm is .845 kg. (sp. gr. is —.655). This corresponds to the average mol. weight of 18.9.

Separate determination for H_2 gives figures varying from those shown in the table by + 15% to—20%; for the total unsaturates—plus 20% to—10%. The nitrogen determinations give variations from 0 to plus 3%; for oxygen and carbonoxide determinations—from 0 to 1.5%. The quantity of Carbon dioxide was obtained only once as .2%

TABLE 11

	% By Volume		% By Weight	
Hydrogen	22.0		2.4	
Saturated Hydrocarbons with av. mol. weight of 18.2—				
Methane	43.4		36.5	
Ethane	8.0	51.4	12.5	49.0
Nitrogen		1.2		2.9
Oxygen and Carbonoxide		.4		.6
Unsaturated hydrocarbons—				
Ethylene	17.0		25.2	
Propylene	5.3		12.0	
n-Butylene	1.0		2.9	
Divinyl	0.7		2.0	
1-butylene	1.0	25.0	3.0	45.0
Total		100.0%		100.0%

9. GASES DISSOLVED IN LIGHT CRACKED GASOLINE

As it was previously indicated by one of us,[36] the third fraction is obtained with a content of 25% (by weight in average) of dissolved gases representing hydrocarbons with four carbon atoms mostly. We expect to publish a special report dealing with this product later.[37] The method of investigation of the composition of the gases is partly described by us in one of our other papers.[38] Here we will give only round figures for the gases dissolved in cracked gasoline to obtain total cuts of various gaseous components resulted from cracking naphtha.

We may assume the average composition of these gases (in round figures).

TABLE 12

Saturates (av. mol. weight of 50)	3%
Propylene	4%
n-butylene	35%
Divinyl	18%
Isobutylene	40%[39]
	100%

10. THE TOTAL CONTENT AND CUTS OF SEPARATE COMPONENTS

In Nos. 8, 9, 11 and 12 tables of the last chapters a summary of content of separate components (in per cent by weight) was made for the three fractions of rectification of cracked gases. According to

process data, we can accept the following distribution of our gases by fractions (by weight).

Fraction of fixed gases.....	20 %
Fraction of wet gases.....	76.5%
Gases dissolved in light cracked gasoline	3.5%
	100.0%

The production of gas (without vapors of gasoline) from the raw material subjected to destructive distillation can be assumed as 33% by weight (for Soorahan topped crude and under normal process conditions). During the production of gasoline with a triple charging stock (up to 45-50 kg. per hour) the production of gas is reduced to 24% and even to 20% by weight of the raw material. Therefore, in the final table, No. 13, we give two columns —one for gaseous and the other for gasoline. In any case the composition of gases differs only slightly provided the operating temperatures are the same.

TABLE NO. 13—COMPOSITION OF GASEOUS COMPONENTS

	By Fractions				Production of Gases from the Raw Material	
	Fixed Gases	Wet Gases	Light Gasoline	Total of Gaseous Products of Cracking	Gases	Gasoline
	Per Cent by Weight in Respect to Gases				Per Cent by Weight	
Hydrogen	2.4	0.2	...	0.7	0.23	0.17
Saturated Hydrocarbons	49.0	29.6	3.0	32.5	10.77	7.80
Unsaturated Hydrocarbons	45.1	69.8	97.0	65.8	21.90	15.80
INCLUDED IN THE ABOVE:						
Ethylene	25.2	17.1	...	18.1	6.1	4.3
Propylene	12.0	24.3	4.0	21.1	7.1	5.2
Normal Butylene	29.	9.0	36 0	8.7	2.9	2.1
Divinyl	2.0	6.6	18.0	6.1	2.0	1.4
Isobutylene	3.0	10.3	40.0	9.9	3.3	2.4
Vapors of Unsaturated Gases with five or more carbon atoms	...	2.5	1)	1.9[2])	0.6[2])	0.4[2])
N_2, CO_2, O_2	3.5	0.4	...	1.0	0.30	0.23
	100%	100%	100%	100%	33.2%	24.0%

In all cases the dominant position is held by the unsaturates forming almost two thirds of the whole weight of the gas. Out of the unsaturates, those with four carbon atoms form the majority,—24.7% by weight of all gases (or 37.6% by weight of the unsaturates); there are just as many unsaturated hydrocarbons with three carbon atoms,—in form of only possible propylene, 21.1% by weight of total gas (or 31.0% by weight of the unsaturated portion). Figure for ethylene is 18.1% (or 27.5% of unsaturates), only somewhat less than that for propylene. Therefore, it can be said, that in our gases there are about equal amounts of the unsaturates with two, three and four atoms of carbon.

Deductions of this work are given directly in different parts of the text, and we are not going to repeat them. However, we wish to convey some thoughts of a general character. As it is seen, the gases, studied by us, are very rich in unsaturated hydrocarbons. The quantities of separate olefins are higher than those obtained when making toluol by pyrogenitic process, etc. The practical absence of other components, besides CH_4, C_2H_6 and H_2, allow us easily to get rectified fractions with a high concentration of one of the olefins.

We must forget that the gas from vapor phase cracking is an unpleasant waste,[40] a production loss, etc. Such a great quantity of gas and its composition must be considered as an advantage.

The gas from vapor phase cracking is the richest and easiest source of raw material for chemistry. So far chemical technology has not found anything similar to it (for synthesis of derivatives of the wet series). These gases may be a basis of manufacturing of a series of chemical products up to the finest pharmaceutical preparations.

The burdensome waste opens a new page in history of crude oil, and it will not be long before this waste will take the right place, when it will become a key product for which special plants will be built, and which will create a new branch of chemical industry.

THE LABORATORY OF
"NAPHTHA GAS,"
Leningrad Chemical Trust.

[32]"Petroleum Industry" No. 10, page 574, 1925.

[33]It is possible to accomplish the rectification either at a higher pressure with a temperature higher than +10°C in the dephlegmator or at a normal pressure but at low temperatures. The first method is very simple and economical and can be accomplished in moderate scale, the second method can be performed only in small laboratory scale. This method is described by the same authors in "About Action of Sulphuric Acid", etc. Both methods are entirely satisfactory, but the rectification is better and the control is easier with the second method.

[34]See our report, mentioned above, at Mendeleev Congress.

[35]Euel. Res. Tech. Paper No. 19.

[36]"Petroleum Industry" N 1, 1929; also see S. Brichs "Oil and Gas Journal," 17/V, page 164, 1928.

[37]In the same time with B. G. Moor and D. A. Cherniav.

[38]"The effect of Sulphuric Acid on Lightest Products of Cracking Oil", Chapter 1.

[39]During 1929 it was noticed that the content of isobutylene was getting down to 28% and divinyl and n-butylene increasing to 20% and 45% respectively. But since all other material was obtained, 1927 and 1928, the following calculation is based on Table No. 10.

[40]"All refineries considered this gas as a fuel exclusively." (A. F. Dobriansky "Petroleum Industry" N 642, 1923.)

[41]Also see Danis "Ind. Eng. Chem." p. 844, 1926; De Florez, "Refiner", p. 71, January, 1928; G. Crume "Ch. Met. Engng.", 25, 907, 1921; Fanning "Oil and Gas Journal" 12/V. pp. 66, 1924; H. A. Cedih, "Petroleum Industry" N 11-12, 1928; Ritketly, also Brooks "J. Inst. Petr. Techn.", p. 38, 1920; J. Norris, "Ind. Eng. Chem.", 324, 1927, etc.